NISTIR 6312

Interactions of Polymers with Fillers and Nanocomposites, NIST, June 18-19, 1998: A Workshop Report

Alamgir Karim

Acknowledgments
Alan Nakatani
Kathy Barnes
Brett Ermi
Jack Douglas
Erik Hobbie
Eric Amis

NIST

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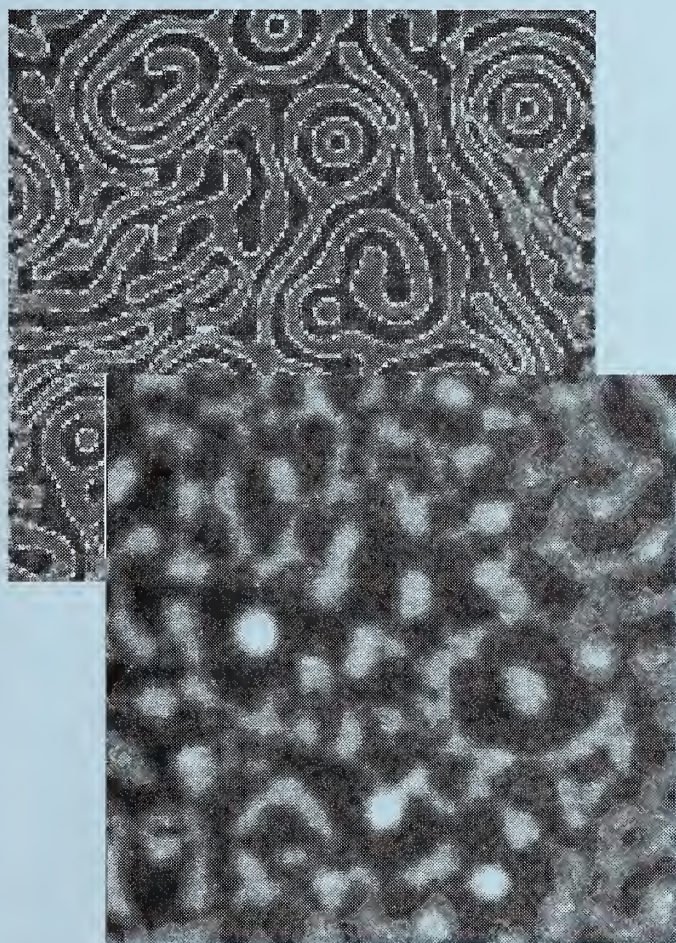Acknowledgments
Alan Nakatani
Kathy Barnes
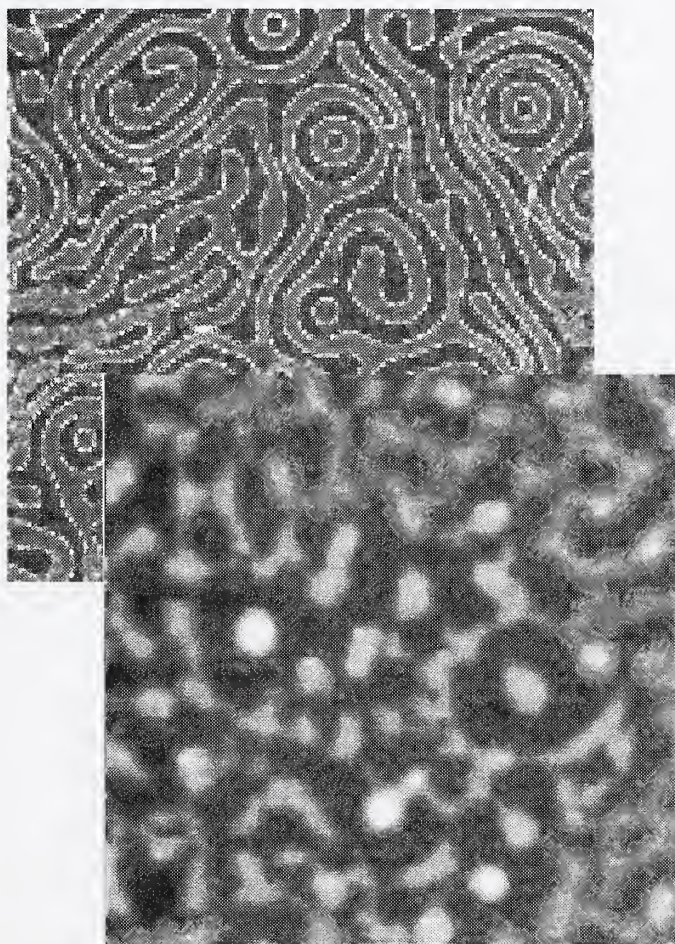**Brett Ermi**
Jack Douglas
Erik Hobbie
Eric Amis

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Institute of Standards
  and Technology
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INTRODUCTION

Filled polymers and nanocomposites represent a significant share of the world plastic market, competing strongly with costly high performance plastics. Yet, a major limitation to the potential growth and development of this industry has been a lack of understanding of the interactions between fillers and the polymer matrix and of measurements quantifying such interactions. This limitation has forced the filled polymers industry to adopt empirical approaches for product development, a procedure that necessarily delays product development cycles. Recently, renewed interest in the area of clay nanocomposite materials has spurred a number of industries to initiate research programs for developing applications of these materials. A long term plan for successful application of nanocomposites as materials with unique properties also requires fundamental characterization measurements. Thus, the need to identify critical technology development and state of the art measurement techniques to support the rapid growth of the filled polymers industry is generally recognized as being important.

1.1 Workshop Objective

Problems, Opportunities and Challenges in Filled Polymers

The NIST workshop entitled "Interactions of Polymers with Fillers and Nanocomposites" sought to gather experts on filled polymers and nanocomposites from industry and academia to identify the most critical issues hindering progress on filled polymer technology. Over two days the workshop participants highlighted important scientific and technical problems with the aim of identifying critical measurement techniques and modeling which can improve the performance, manufacture, and applications of filled polymers and nanocomposites. The recommendations of the workshop were used to better define the research efforts of the Polymer Blends and Processing Group in the area of filled polymers and nanocomposites, in addition to laying the foundation for collaborations with industry.

1.2 Executive Summary

Control of *molecular-level interactions* and measurement of *polymer dynamics* at the filler interface were identified by participants at a recent NIST sponsored workshop as the most critical issues in filled polymers and nanocomposites. Although filled polymers already represent a substantial fraction of polymer materials, recent developments in nanocomposites have attracted renewed interest in developing the science and technology base to optimize performance. The workshop focused on identifying the most critical issues hindering improvements in applications of filled polymers and nanocomposites. Of the 75 external participants, 50 were from industry, mostly experts in the area of filled polymer technology. Through productive discussions, the workshop participants highlighted and prioritized a range of future research and measurement needs for filled materials.

The discussions also laid the foundation for future research in this area, and collaborations between NIST, industry, and academia. The Polymer Blends and

Processing Group of the Polymers Division, MSEL initiated research on polymer-filler interactions in 1997 using X-ray, neutron and light scattering in combination with microscopy techniques, and concepts that had been previously applied with great success on polymer blends. The results of the workshop will be used to plan future directions of the NIST work.

1.3 Acknowledgements

The authors would like to thank the speakers for their valuable presentations, and the session coordinators for conducting the meetings of the workshop. In addition, we would like to thank the participants for attending and contributing to the discussion sessions. Furthermore, we would like to express our appreciation to the Conference Facilities Group at NIST for providing the arrangements and organization that made the workshop possible.

1.4 Disclaimer

Commercial equipment, instruments, software, materials or services are identified to adequately report the presentations and discussions that took place. Such identification does not constitute nor imply recommendation, endorsement, or criticism by the National Institute of Standards and Technology (NIST). Nor does NIST take responsibility for the accuracy or source of the various non-NIST numerical values reported in this document, or the use of units other than those of the International System by non NIST authors.

PRESENTATIONS SUMMARY

2.1 Opening Remarks

Dr. Leslie Smith (MSEL Director)
The Materials Science and Engineering Laboratory (MSEL) director, Dr. Leslie Smith emphasized the importance of fillers and nanocomposites to the polymer industry and the need for fundamental measurements in the area. Dr. Smith described the laboratories structure under MSEL and also the different NIST programs, placing emphasis on the Advanced Technology Program and the Measurements and Standards Laboratories. The ways by which NIST identifies needs were summarized: 1) Visits to and by industrial researchers; 2) Through workshops organized by NIST; and 3) Through industrial roadmaps.

Dr. Eric Amis (Group Leader, Polymer Blends and Processing Group)
Dr. Eric Amis described the goals of the Polymer Blends and Processing Group and emphasized that the area of filled polymers and nanocomposites was becoming a high priority area for research by this group at NIST. He iterated the purpose of the workshop as gathering the experts in the area of filled polymer technology to highlight the key areas and critical issues hindering progress in the area. The ideas generated through the Workshop would be used guide the blends research efforts at NIST and potentially establish long term collaborations with industry in some critical areas.

Dr. Alamgir Karim (Physicist, Polymers Blends and Processing Group)
Dr. Karim discussed the Blends and Processing Group research program in the area of filled polymers to study fundamental aspects related to measurements of filled polymers and nanocomposites. He described the nature of research being conducted by the group in the area of filled polymers and nanocomposites that take advantage of some unique measurement capabilities at NIST.

2.2 Compounding, Reinforcement and Toughening Session (I)

"Concepts in Rubber Chemistry: The Role of the Filler particle", Gary T. Burns, Dow Corning Corp., Pare Industriel-Zone C, Seneffe B-7180, Belgium

Dr. Burns gave an overview of filled polymer processing technology and discussed properties of fillers that impact material characteristics. One of the problems with elastomers is that they change during compounding so that the initial and final state elastomers are quite different. He emphasized that while much has been done to characterize fillers prior to processing, the state of the filler in the final product is poorly characterized. Also discussed were the two main features controlling properties of the filled materials: Filler structure/geometry and the surface energy.

Regarding filler structure/geometry the primary particle size is the most important contribution to the surface area. The size of typical primary particles is in the range of (3 to 50) nm. In this regard, the measured surface area by gas adsorption may not be the true surface area. The aggregation of the primary particles and packing control porosity,

and hence spatial arrangements of particles within aggregates and of the agglomerates are important. However, while the role of aggregation is important, there is no well defined measure of its reinforcement properties. Additionally, the density makes a difference and is important.

Surface area can be measured by BET (N_2 adsorption) and CTAB adsorption. The relevant formulas for obtaining the surface area of spheres and rods were discussed. Pore volume can be measured by BJH analysis, mercury porosimetry, and dibutyl phthalate absorption. The role of surface roughness is system specific, which implies that there are surface energy effects, so that the measured surface area may not be related to the true surface area.

Concepts of bound and occluded rubber were introduced as measures of polymer-filler interaction. The bound rubber are the rubber molecules which are strongly adhered to the filler surface, while the occluded rubber are the polymer chains trapped in voids of aggregates and are shielded from the applied stress. The bound rubber has a layer of directly attached chains and a second layer of entangled chains. Shape factor could be related to occluded rubber. Bound rubber fraction can be measured by NMR techniques as well as by extraction. All such measurements seem to provide satisfactory results.

On the theoretical side, Dr. Burns discussed the Modified Smallwood-Guth-Gold Equation for predicting the modulus of a filled material as a function of filler volume fraction only.

In his concluding remarks, he stated the following needs for advancing the understanding of filled polymers: 1) Development of a generalized equation with well-defined variables such as filler shape, filler porosity, filler-filler and filler-polymer interactions; 2) Accepted techniques to measure these variables; 3) Characterization of the state of the filler not only before but after mixing as well.

Discussion- The point was raised that occluded and bound rubber are related to hysteresis behavior and that rheological effects often differ from observed mechanical behavior.

Select Figures

Factors Contributing to Reinforcement

- Surface Area of Filler
- Aggregate Structure
    - Porosity (inherent and in-situ generated)
    - Shape (probability of filler-filler contact)
- Surface Energy
    - Polymer-Filler Interactions
    - Filler-Filler Interactions

Fig. 1

Individual Particles Interacting with
Each Other

Individual Particles Interacting with
Polymer Matrix

Particles adhering through entanglements
of adsorbed polymer

Particles adhering through sharing of
adsorbed polymer

Fig. 2

Dow Corning

FILLERS

POLYMER CHAINS

Primary Particle
(3-50 nm)

Polymer Cross-section
(~2-10 nm^2)

Aggregate
(100-200 nm)

Random Coil (~ 10-50 nm)

Agglomerate
(10^4 - 10^6 nm)

Block Copolymer
(10-100 nm domains)

Dow Corning

Fig. 3

Primary Particle Size Versus Surface Area for Silica Particles

For aggregated spherical particles the surface area available to a nitrogen probe is reduced by:

$$SA = S_0(1 - 0.354n/4r)$$

n = no. of particle contacts
r = radius (nm)
d = density (g/cm³)
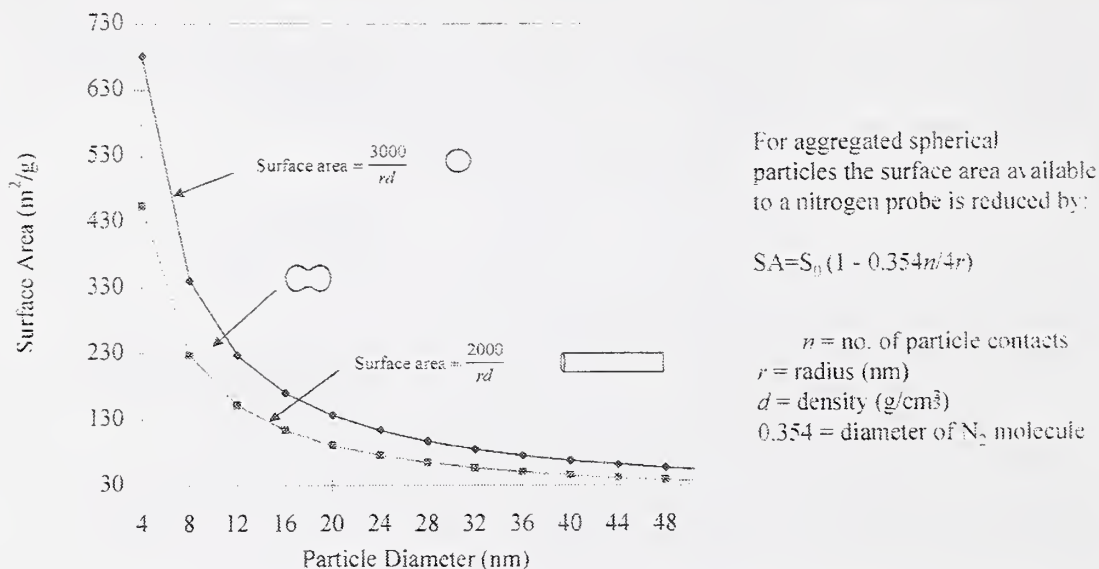0.354 = diameter of N_2 molecule

Fig. 4

Filler / Aggregate Structure

Structure or Geometric Parameters:

Surface area - Defined by the shape and size of the primary or ultimate particle
- BET analysis (N_2 adsorption)
- Hexadecyltrimethylammonium bromide (CTAB) adsorption

Internal void or pore volume - Defined by the packing or coordination number of the ultimate particle
- BJH anlysis (N_2 adsorption)
- Hg porosimetry
- Dibutylphthalate (DBP) Absorption
- Pore Volume = $1/\rho_{bulk} - 1/\rho_{true}$

Shape Factor / Aspect Ratio

-Medalia, *J. Colloid Interface Sci.*, 24, 393 (1967)
Medalia, *ibid.* 32, 115 (1970)

OCCLUDED RUBBER - Rubber which is situated within the irregular contours of an aggregate and is thus shielded from an applied stress. The presence of occluded rubber increases the effective volume fraction of filler. For carbon blacks,

$$\phi_{ie} = 0.5\phi[1 - \left(\frac{1 + 0.02139(DBPA)}{1.46}\right)]$$

—— *Dow Corning*

Fig. 5

Surface Differences between Silicas and Carbon Black

Silica

Carbon Black

Concentration of Silanol is fairly
constant (4-6/nm²)
-Fumed (30-40 % isolated / 60-70 % vicinal)
-Precipitated (predominantly vicinal)
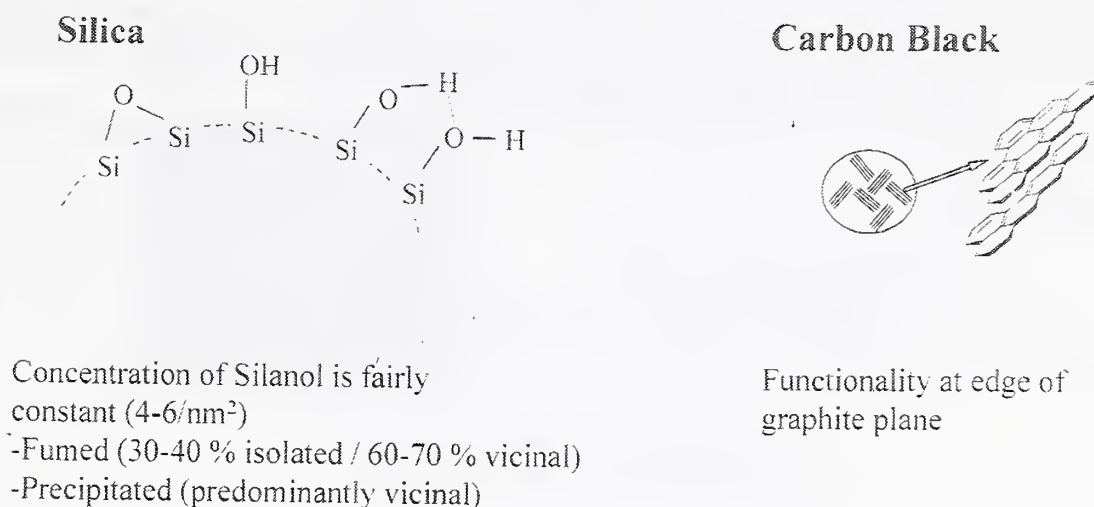
Functionality at edge of
graphite plane

Fig. 6

Needs

General Equation with clearly defined, *measurable* variables
- filler shape (probability /perculation factor)
- filler porosity (effect of pore volume, pore shape
and pore size distribution)
- filler-filler interactions (γ_s^{s})
- filler-polymer interactions (γ_s^{d})

Accepted/Standardized Techniques to measure variables

State of Filler Before and After Mixing

Fig. 7

"Dynamic Studies of Compounds-Latest Results", Henry Yang, M. Gerspacher and
C.P.O' Farrell, Sid Richardson Carbon Co., Fort Worth, TX

Dr. Yang discussed the role of filler distribution on high and low frequency
rheological behavior. He stated that carbon black has no porosity or surface groups and
that the crystal edges in the particles are the active sites. Nevertheless, there are a

number of different interactions, which need to be identified and quantified, and the relevance of each interaction needs to be determined.

The high frequency behavior is dominated by the polymer while the low frequency behavior is dominated by the filler properties. Increasing filler dispersion lowers reinforcement while it increases the attenuation coefficient. Low strain, low frequency behavior can be related to the filler-filler interactions and low strain, high frequency behavior can be related to the filler-polymer interactions.

Discussion- Questions were raised concerning the lack of surface groups and porosity in carbon blacks.

Select Figures

Dynamics of Tread Compounds

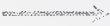Tire treads undergo periodic deformations
Two Domains of Strain Energy Input

A. Wheel Assembly
· Frequency < 40 Hz
· Tread deformation (strain) between .1 and 20 %

B. Tire/Road Contact
· Very small tread volume involved
· Very small strain
· Very high frequency (MHz +)

Strain and Frequency are Essential Parameters

806F003F

Fig. 1

Tire Tread Requirements

Good Rolling Resistance	Low Heat Generation in (A)
Good Traction	High Energy Adsorption in (B)
Good Wear	Complex Mechanism

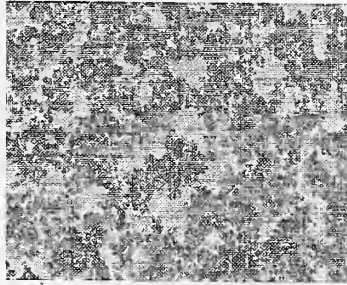Low Hysteresis at Low Frequency

High "Hysteresis" at High Frequency

Ideal Tread Compound

806F004F

Fig. 2

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Tire Tread Compounds

Main Components

* Elastomers

      Crosslinked Networks
      Polymer Chain Mobility

* Filler (Carbon Black)

      (Percolated) Network
      Ridgid Filler Aggregate

Materials Interactions

Fig. 3

806F005F

Interactions
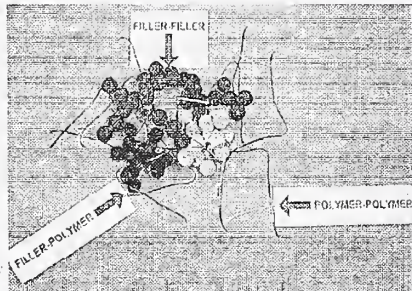
Filler - Filler Interaction

Polymer - Polymer Interaction $\begin{cases} \text{X Link} \\ \text{Others} \end{cases}$

Filler - Polymer Interaction

Type of Interaction		
* Van der Waals	→	Carbon Black Network
		Carbon Black - Polymer
* Chemical/Covalant	→	Surface Crosslink
* Electrostatic	→	Polymer Chains
		Carbon Black - Polymer (?)

Amount of Interaction
* Filler Morphology and Dispersion
* Crosslinking Density
* Polymer Type

Interactions Relevancy ?

806F009F

Fig. 4

Strain Energy and Interactions

* Low Frequency
* Strain Range below 30%
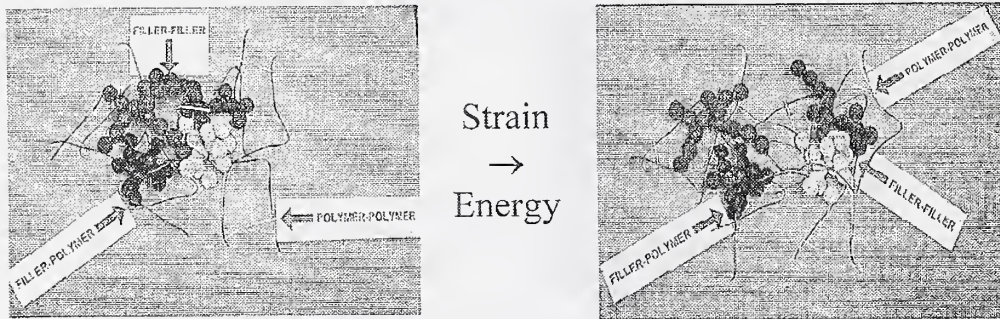
Strain
$\rightarrow$
Energy

- Carbon Black Network $\rightarrow$ subnetworks
- Polymer Chains $\rightarrow$ $(t_R \sim t_E)$ relaxation

Carbon Black Network Dominates

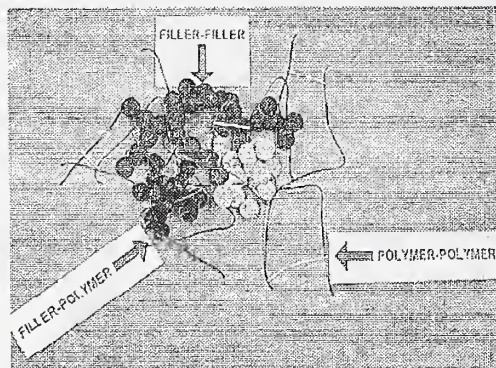806F010F

Fig. 5

Strain Energy and Interactions (Cont'd)

* High Frequency (MHz)
* Very Low Strain

- Carbon black network not disrupted

- Only short polymer chains segment relax

Polymer Network Dominates

806F011F

Fig. 6

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Future Evaluations

* Effect of shear rate

* Effect of temperature

* Effect of substrate
  - nature
  - roughness
  - dry / wet

Develop Meaningful Testing
Parameters

Fig. 7

"Flow-induced Microstructural Changes in Filled Polymeric Liquids", Saad A. Khan, Srinivasa R. Raghavan, Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695-7905
One of the aspects of interest in filled systems is to elucidate microstructural changes caused by flow fields, and to evaluate whether these changes persist over long periods of time. This point becomes particularly relevant in non-traditional composite systems where the particle/filler interactions can lead to a wide range of rheological behavior, such as in fumed silica systems in low molecular weight polymers. In fumed silica systems, the surface characteristics can be tailored to give rise to two different classes of filled materials: (a) colloidal gels (networks); and (b) colloidal (stabilized) suspensions. In the case for gels, a three-dimensional network of colloidal (fumed silica) particles extends throughout the volume of the system. Under the action of oscillatory pre-shear at large deformations, the microstructure is disrupted into distinct entities. The critical variable is not the shearing time but the strain amplitude. The equilibrium microstructure can be changed with pre-shear and shows anomalous behavior in terms of the existence of a minimum in the recovered dynamic elastic modulus ($G\square$) when examined as a function of pre-shear strain amplitude. To better understand the changes occurring during shear, the concept of fractal dimension was introduced. Changes in the power law behavior of $G\square$ and the critical strain amplitude versus filler volume fraction was observed following preshear. This could be related to changes in fractal dimension from 1.75 before shear to 2.02 following moderate preshear. While the fractal dimension before shear was experimentally obtained, that following shear was obtained using the model of Potanin et al. and requires further experimental verification.

In the case of stabilized suspensions, a dramatic increase in steady-shear viscosity was observed at high shear-rates (shear-thickening). Likewise, a dramatic enhancement in the dynamic properties (complex modulus G^* or complex viscosity η^*) was also observed under large oscillatory deformations and high frequencies – a phenomenon

referred to as strain-thickening. A unique correlation between steady shear-thickening and dynamic strain-thickening was established utilizing a "modified Cox-Merz rule." While these shear and strain thickening behavior are consistent with the formation of hydrodynamic clusters, direct evidence of microstructural rearrangements during shear would be highly desirable.

Discussion- The role of particle and orientation and utility of techniques such as rheo-optics was raised. Since the structures are not anisotropic, it was doubtful there would be much orientation, hence the rheo-optical techniques would not be very useful.

Select Figures

Overview
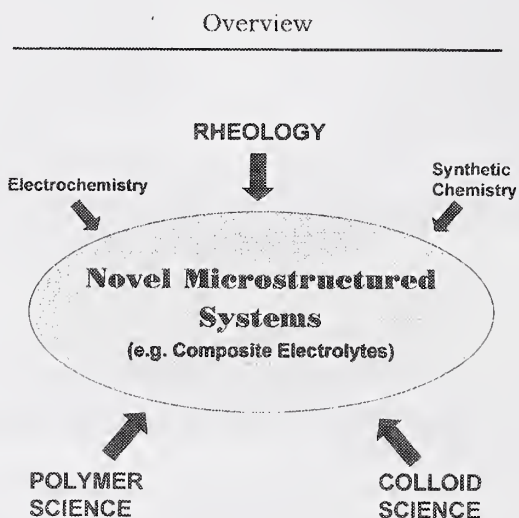
Fig. 1

Polymer Electrolytes for Lithium Batteries
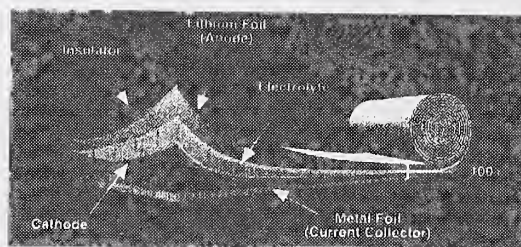
Material Requirements

- Acceptable ionic conductivity (>10^{-3} S/cm at 298K)
- Chemically and electrochemically stable
- Mechanically stable (solid-like at end-use conditions)
- Processable

NEED TO TAILOR RHEOLOGY AND MICROSTRUCTURE

Fig. 2

Composite Polymer Electrolytes (CPEs)

$\sim\!\!Si\text{-}OH$

$\sim\!\!Si\text{-}C_8H_{17}$

Fumed Silica (FS)
(Tailored Surface Chemistry)

+

Poly(ethylene glycol) (PEG-dm),   Lithium salt
(low mol.wt.; end-capped)   (e.g. Li imide)

GEL (*Physical*)
(Mechanically Stable, yet processable)

Fig. 3

Fundamental Issues

Objectives
- Equilibrium Microstructure ◄
- Behavior Under Shear ◄

Fig. 4

COLLOIDAL GELS

- Show anomalous recovery behavior on being subjected to oscillatory shear at moderate strains.

- Attributed to changes in fractal dimension due to shear

COLLOIDAL SUSPENSIONS

- Show shear-thickening under steady shear and strain-thickening under oscillatory shear. The two phenomena can be correlated by an extended Cox-Merz rule.

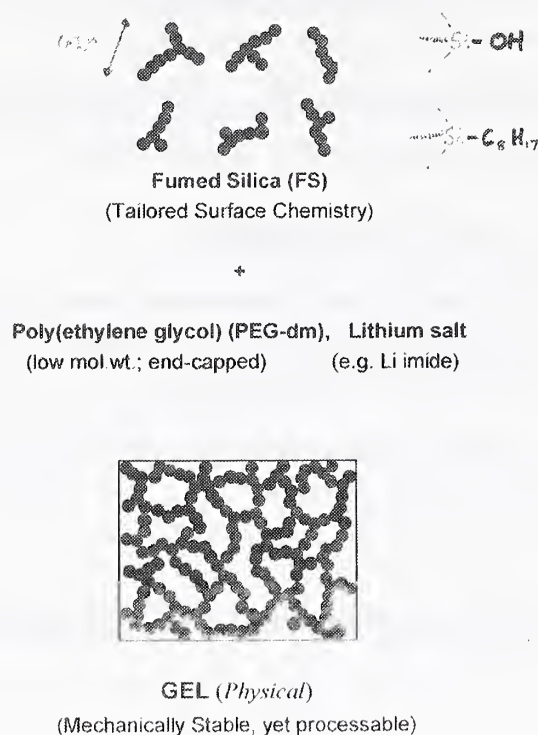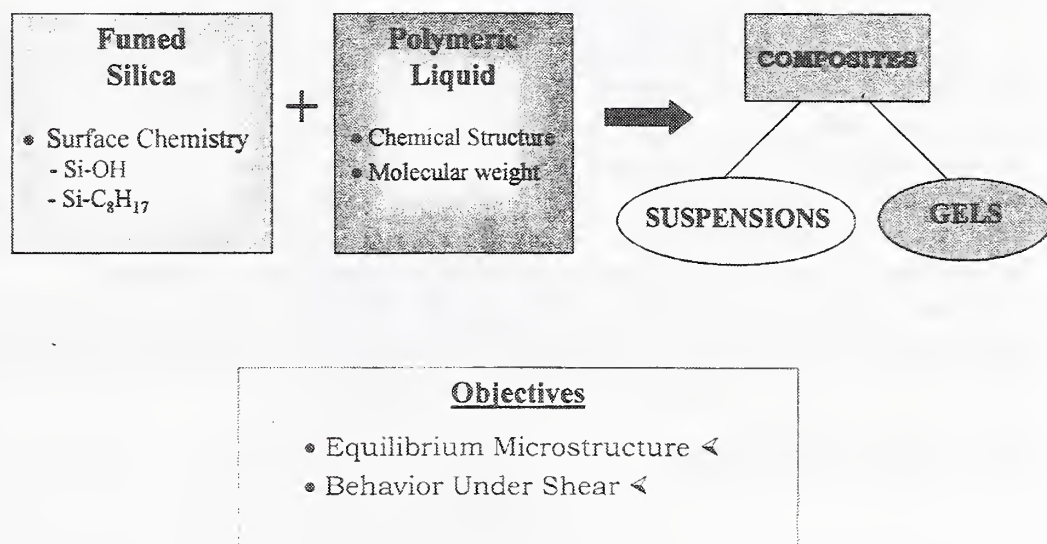- Both phenomena are attributed to hydrodynamic forces which induce cluster formation

Above hypotheses need to be experimentally verified.

Fig. 5

"Recent Industrial Developments: From Anti-Static Polymers to Artificial Marble", Moshe Narkis, Dept. of Chemical Engineering, Technion, Israel Institute of Technology, Haifa, Israel

Dr. Narkis commented that while compression molding studies are available in the literature they are of little interest to industry. This is because injection molding is typically used in industry and so these types of studies are preferred by industry. He stated the need for new anti-static injection moldable composites since most current materials become insulating when they are injection molded. He illustrated these ideas with carbon black, glass fibers, and polypropylene (PP) with 3 other component fillers. Finally, he urged the need to better understand multicomponent (greater than 3) immiscible systems and stated the need for better conductivity definitions.

Discussion- Question was raised concerning the possibility of measuring the conductivity during and after processing. Another question was raised concerning the effect of carbon black structure on its capacity to migrate.

Select Figures (Next page)

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CARMELSTAT™

The Unique 10^6 - 10^9 ohms/sq ESD Material with Only 1% Carbon Black

- About 1% carbon black provides permanent, controllable, consistent resistivity
- Controlled stiffness / impact balance
- High Heat Deflection Temperature
- Low-sloughing, clean room compatible
- Cost - effective

CARMEL OLEFINS   *R&D Department*

Fig. 1

THE BEHAVIOR OF CARBON BLACK / MISCIBLE POLYMER BLENDS IS SIMILAR TO CARBON BLACK / SINGLE POLYMER SYSTEMS. IN CONTRAST THE DISTRIBUTION OF BLACK PARTICLES IN AN IMMISCIBLE POLYMER BLEND IS MUCH MORE COMPLEX.
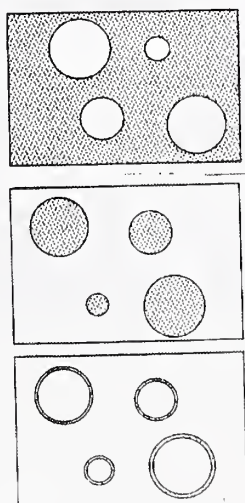
Fig. 2

FOR A GIVEN POLYMER, THE TRANSITION

DEPENDS ON THE TYPE OF CARBON BLACK

$DBP_I > DBP_{II} > DBP_{III}$
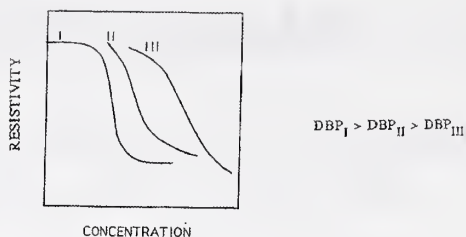
FOR A GIVEN CARBON BLACK, THE

TRANSITION DEPENDS ON THE POLYMER

TYPE. THE CRITICAL PERCOLATION

CONCENTRATION CAN BE CORRELATED WITH
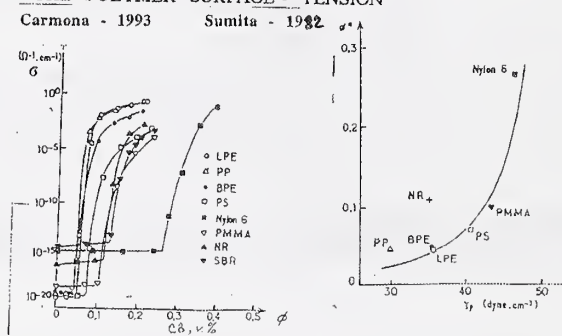
THE POLYMER SURFACE - TENSION

Carmona - 1993   Sumita - 1982

Fig. 3

Resistivity vs. Carbon Black Loading --

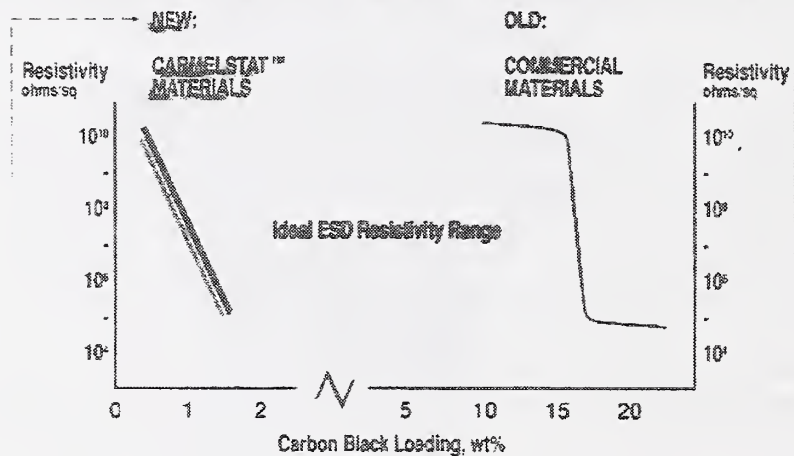**Fig. 4**

COMPARISON OF INJECTION MOLDED COMPOSITES AND
COMPOUNDS WITH COMMERCIAL MATERIALS

POLYPROPYLENE

Property	PP/GF/CB	PP/CB	PP/CF	PP/CF	PP/CB Commercial	PP/CF Commercial
Conductive Filler, %	1.2	6	10	15	>15	>15
Tensile Strength, MPa	55	38	41	22	41	
Flexural Modulus, MPa	3300	2910	5275	6508	1240	4300
Izod Impact, notched, J/m 23°C	57	13	43	50	180	54
Heat Distortion Temperature, °C	161	95	143	147	115	132
Volume Resistivity, ohm-cm	$10^6 - 10^7$	$<10^3$	10^3	$<10^3$	$10^2 - 10^6$	$10^2 - 10^5$
Surface Resistivity, ohm/sq	$10^6 - 10^7$	$<10^3$	10^3	$<10^3$	$10^2 - 10^6$	$10^2 - 10^6$

POLYCARBONATE

Property	PC/GF/CB	PC/CB	PC/CF	PC/CB Commercial	PC/CF Commercial
Conductive Filler, %	2	6	15	>15	>15
Tensile Strength, MPa	96	52	136	65	145
Flexural Modulus, MPa	5150	2888	8715	3100	8960
Izod Impact, notched, J/m 23°C	45	50	58	53	150
Heat Distortion Temperature, °C	144		140	132	150
Volume Resistivity, ohm-cm	$10^6 - 10^7$	$<10^3$	$<10^3$	$10^2 - 10^6$	$10^2 - 10^5$
Surface Resistivity, ohm/sq	$10^6 - 10^7$	$<10^3$	$<10^3$	$10^2 - 10^6$	$10^2 - 10^6$

PBT

Property	PBT/GF/CB	PBT/CB	PBT/CF	PBT/CB Commercial	PBT/CF Commercial
Conductive Filler, %	1.5	6	15	>15	>15
Tensile Strength, MPa	61	56	126	54	103
Flexural Modulus, MPa	6120	3130	8940	4600	9655
Izod Impact, notched, J/m 23°C	70	30	51	110	48
Heat Distortion Temperature, °C	224	194	224	202	225
Volume Resistivity, ohm-cm	$10^6 - 10^7$	$<10^3$	$<10^3$	$<10^3$	$10^2 - 10^6$
Surface Resistivity, ohm/sq	$10^6 - 10^7$	$<10^3$	$<10^3$	$<10^3$	$10^2 - 10^6$

Fig. 5

WHAT IS NEEDED ?

- A BETTER UNDERSTANDING OF THE GENERAL BEHAVIOR OF IMMISCIBLE MULTI-COMPONENT SYSTEMS.

- BETTER DEFINITIONS OF CONDUCTIVITY LEVELS FOR THE VARIETY APPLICATIONS OF CONDUCTIVE MATERIALS

- A GOOD BACKGROUND IN POLYMER BLENDING, RHEOLOGY AND PROCESSING OF SHORT-FIBER COMPOSITE MATERIALS AND ABOVE ALL, *IMAGINATION* !!!

Fig. 6

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2.3 Compounding, Reinforcement and Toughening Session (II)

"A comparative study of microstructure and fracture behavior of a conventional filled polymer and a nanocomposite", Albert F. Yee, J.P.Harcup, J. Du, and J. Lee, Dept. Materials Science & Engineering, The University of Michigan, Ann Arbor

This talk focussed on fracture and toughening mechanisms in macro and nanocomposite materials. One of the goals of this research work on fracture and toughening was to explore the size scale of interfacial properties. Dr. Yee mentioned that there was a lack of theoretical models for satisfactorily explaining toughening of filled materials. This is a different approach than what most traditional filled systems entail. Instead of a rigid particle in a rubbery matrix to get enhanced modulus (amongst other properties), one has a rigid matrix filled with rubbery particles to get improved fracture resistance. He elaborated on crack shielding and crack pinning in this context. The idea of bound rubber becomes important as well for toughening. It was also noted that better dispersion does not necessarily lead to better properties and he stated the need to examine the dynamics of processes to get an understanding of the mechanics involved. In this regard, measure of the morphology alone is insufficient to understand fracture and toughening in filled materials.

Discussion- Questions on the effect of orientation (A: Hasn't been looked at) and the effect of aggregation on the interface (A: Not sure).
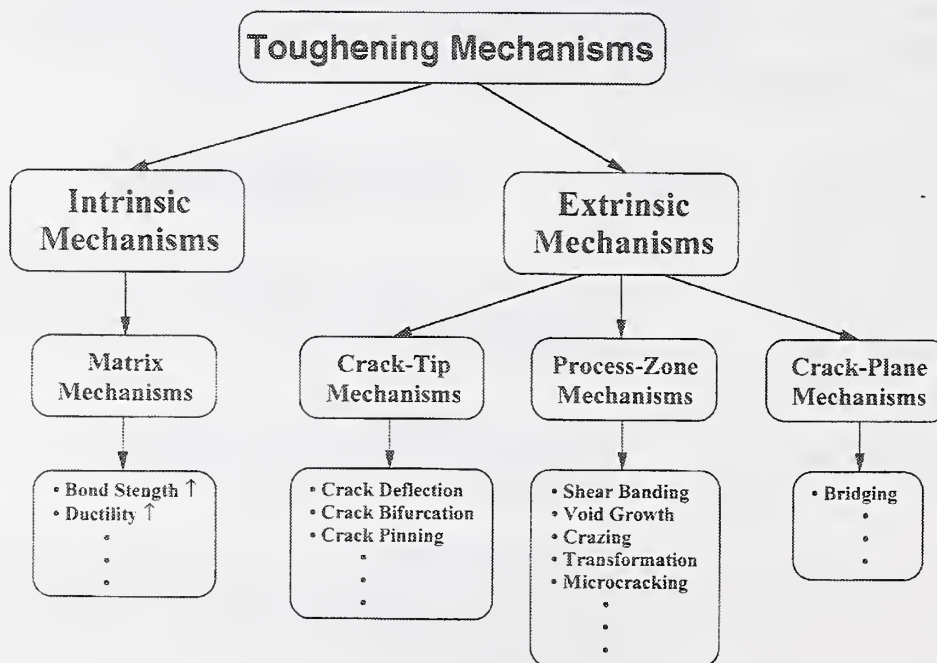
Select Figures

Fig. 1

Fracture Toughness

— **Homopolymer:** Bond Strength, Cross-link Density, Crystal Structure, ... ◄— Intrinsic Mechanisms

— **Polymer Blends and Composites** ◄— Extrinsic Mechanisms

⌐— Basic Model Systems —⌐

Modulus of Inclusion
>> Modulus of Matrix

Modulus of Inclusion
<< Modulus of Matrix

—e.g. Glass Beads

—e.g. Rubber

Approach

Epoxy/ Glass beads Composites

K_{IC} (critical stress intensity factor) Measurement :
3-PB Fracture Toughness Test

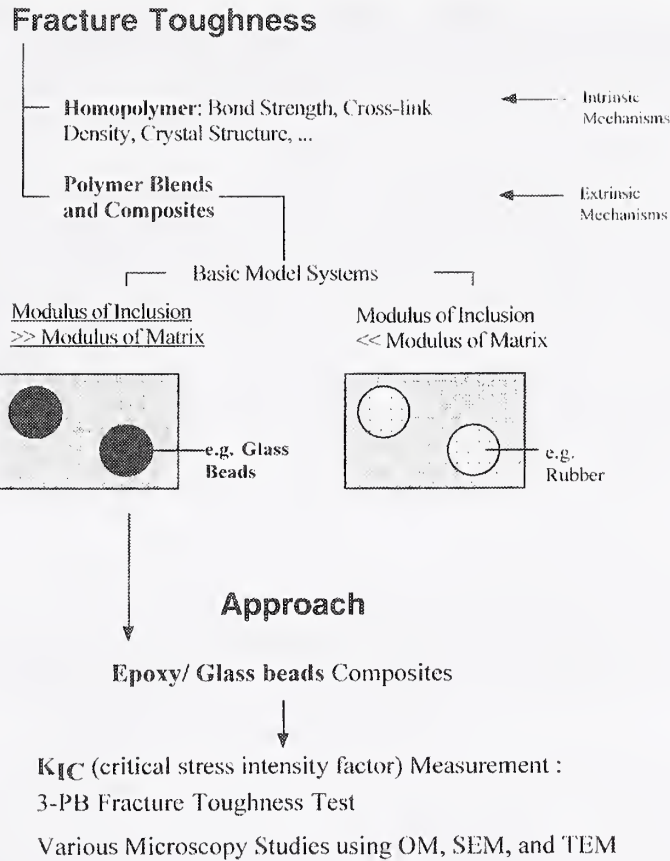Various Microscopy Studies using OM, SEM, and TEM

Fig. 2

Modeling for Steady-State Toughening

- This model is for toughening by shear yielding of the matrix.
- The constituitive behavior (power-law hardening) is for toughened material, NOT for pure matrix.
- A large n (strain-hardening exponent) corresponds to a low hardening material.
- Plane-strain crack-tip field for a power-law hardening material can be described by HRR fomulation.
- Steady-state toughening can be evaluated by an energy-balance approach.

Steady-State Toughening Efficiency

- A significant toughening effect can be obtained only when the ratio of cohesive strength to yield stress (σ_c/σ_0) exceeds a certain value. This can be achieved by decreasing the plastic-flow stress (σ_0) and/or increasing the cohesive strength (σ_c).
- Steady-state toughening efficiency ($\Delta J_{ss}/J_0$) increases with increasing the ratio of cohesive strength (σ_c) to yield stress (σ_0) and/or strain-hardening exponent (n).

Fig. 3

"Metallocene Impact Modifiers: Influence of TPO Paintability and Cohesive Strength", <u>Rose A. Ryntz</u>, Visteon Automotive Systems, Dearborn, MI

Dr. Ryntz talked about crystallization in the presence of fillers. As in the previous toughening problem, the filler particles here are elastomers as well. It was also of interest to study effects of metallocene impact modifiers on cohesive strength of thermoplastic olefins (TPOs). The study involved stability and structure of coatings and the influence of the skin-sublayer interface. Typical measurements involved utilizing compressive shear tests. Also of interest was the effect of having a filler in the presence of two-polymeric components. In Dr. Ryntz's view, for the fillers and nanocomposites area to develop significantly, a knowledge of the mechanical behavior of multicomponent (more than 2) systems was deemed critical. Dr. Ryntz also stated that the needs for the area are interphase characterization and crystallization effects.

Select Figures
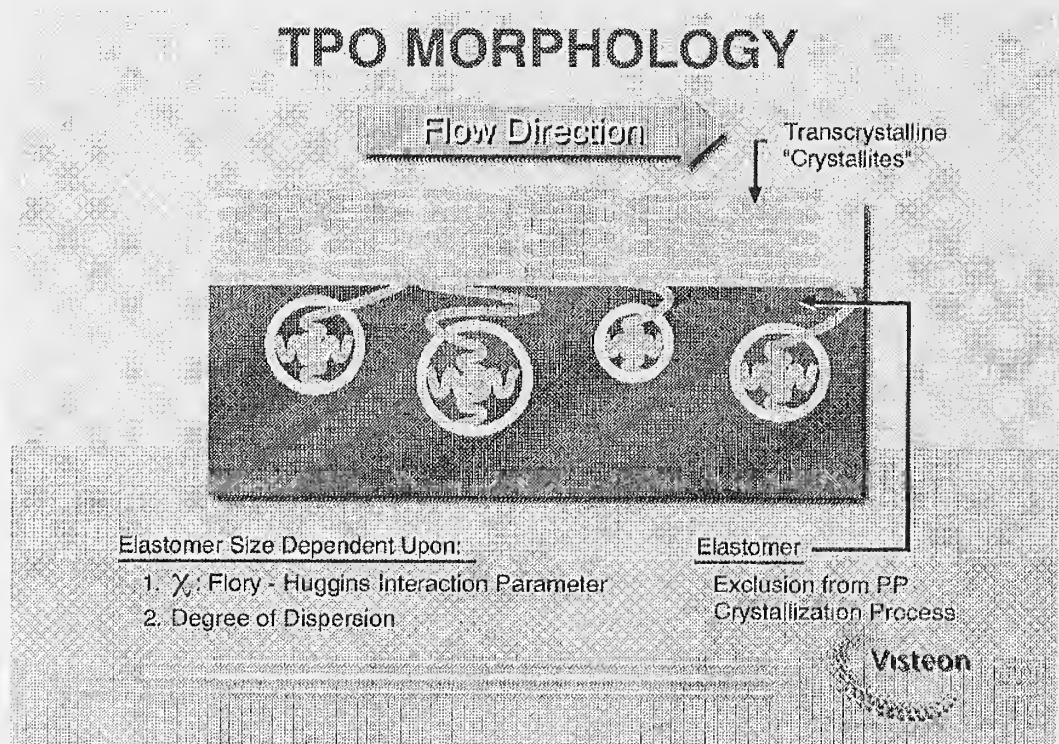
Fig. 1

FACTORS INFLUENCING MISCIBILITY

- Molecular Weight, Molecular Weight Distribution, and Isotacticity Level of Matrix
- Molecular Weight and Molecular Weight Distribution of Elastomer Phase
- Copolymer Ratio in Elastomer Phase
- Concentration of Crystalline/Amorphous Sequences in Elastomer Phase

Visteon

Fig. 2

FACTORS INFLUENCING MISCIBILITY

- Size and Uniformity of Elastomer Dispersion Domains
- Melt Viscosity Ration of Matrix/Elastomer
- Stiffness Disparity, at Meltlike Densities, Between Matrix and Elastomer Phase
- Degree of Entanglement Between Elastomer/Matrix Phase

Visteon

Fig. 3

FACTORS GOVERNING DISPERSION SIZE*

From Melt Blend:

- Rejection of Dispersed Elastomer Particles from Crystalizing Front, Occlusion in Intraspherulitic Regions
- Deformation of Occluded Particles and Rejection Into Newly Formed Boundaries
- Coalescence of Occluded Particles
- Rejection of Particles in Interspherulitic Regions

*Martuscelli, E, Thermoplastic Elastomers from Rubber-Plastic Blends
S.K. De et al Editors, Ellis Harwood, NY, NY 1990 p.39

Visteon

Fig. 4

FLORY-HUGGINS INTERACTION PARAMETER POLY(PROPYLENE) PLASTOMER BLENDS

χ <0.002 Indicative of Miscibility at Mw 100,000

χ >0.002 Made Compatible by Increasing Mw of Dispersed Phase or Partial Crosslinking of Dispersed Phase

χ >>0.03 More Likely for Dispersed Phase to Migrate to Surface

Visteon

Fig. 5

FLORY-HUGGINS INTERACTION PARAMETER*

Plastomer (Solubility Parameter)	Polyolefin (Solubility Parameter)				
	IPP	RCP	ICP	LLDPE	HDPE
	(7.43)	(7.44)	(7.49)	(7.97)	(7.99)
Ethylene-Propylene Elastomer (7.79)	0.023	0.022	0.016	0.006	0.007
Ethylene-Butene Plastomer (7.91)	0.039	0.040	0.032	<0.002	<0.002
Ethylene-Hexene Plastomer (7.94)	0.044	0.042	0.034	<0.002	<0.002
Ethylene-Octene Plastomer (7.96)	0.047	0.045	0.037	<0.002	<0.002
Ethylene-Decene Plastomer (7.94)	0.044	0.042	0.034	<0.002	<0.002
Ethylene-4-Methylpentene Plastomer (7.90)	0.038	0.036	0.030	<0.002	<0.002

Note: Calculations Are Based on Comonomer Content of 35 wt% of Ethylene-Propylene Elastomer, and 20 wt% for Plastomers

*T. Yu, Exxon Chemical

Visteon

Fig. 6

Interphase Characterization Needs

- Develop models with polymer *alloys*
- Determine effects of processing variations
  - Depth dependence
- Compatibility measurement
  - Interphase characterization
- Crystallization effects

Fig. 7

"Blends of Brominated Isobutylene Paramethylstyrene Copolymer (BIMS) and carbon Black", Mun Fu Tse, K.O. McElrath, H.-C. Wang, Exxon Chemical Co., Baytown, TX

In his talk, Dr. Tse discussed the determination of polymer-filler interactions from bound rubber fraction measurements. In these measurements involving carbon black fillers, there is a surface area and concentration dependence. Solvent extractions methods are used to determine the bound rubber content. It was found that the amount of bound rubber is a function of the filler concentration. Blends of a number of different brominated isobutylene paramethylstyrene copolymers (BIMS elastomers) with different types of carbon black were studied. The BIMS elastomers have different levels of BrPMS (bromo-paramethylstyrene) and PMS structure levels. These polymer/filler blends are characterized by solvent extraction at different temperatures (bound rubber fraction), viscoelasticity and stress-strain behavior. It has been found that BIMS elastomer interacts strongly with carbon black, as indicated by bound rubber

measurements. These interactions increase approximately with the specific area of the carbon black, and with the BrPMS and/or PMS content in the BMS elastomer. In some cases, the structure level of the carbon black produces some subtle effects on the stress-strain behavior of the BIMS/carbon black blends.

Discussion- Question concerning whether studies of small molecule model compounds have been done to correlate bound rubber and adsorption / desorption behavior. Also whether calorimetric studies have been done to look at polymer-surface interactions; the need to determine the nature of the binding - whether it is chemical (covalent) or physical.

"Investigations of Filler - Polymer Interactions" A.J. Dias, Exxon Chemical Co., Baytown, TX

Dr. Dias stated that 85 % of elastomers produced are used in tires. Therefore, any incremental improvement impacts a major market segment. In their studies, the driving force behind migration of fillers was investigated. Does the filler move to a specific polymer phase or does the polymer move to the filler were some of the questions being asked. Apparently the filler particles migrated rapidly within and between viscous media, but it was unclear on what the mechanism and driving forces were. In his talk Dr. Dias stressed the importance of studying multicomponent polymer mixtures with filler. He explained that it was not possible to predict properties of networks from structural knowledge because of the range and effects of fluctuations. As an alternate technique to the bound rubber extraction, it was possible to follow adsorption of polymer to filler surfaces from polymer solutions using NMR. The order of addition of the polymers was important, implying the binding may be covalent. Further, he expressed the need to understand the diffusion behavior of polymers near surfaces. In their thin film studies they found that the polymer chains slowed down dramatically in thin films of thickness 20 nm. Additionally, he stated the need to understand the mechanics of deformed filled elastomers. Presently, a model by Lipizzera exists but further extensions and generalizations to filled systems are necessary.

Select Figures

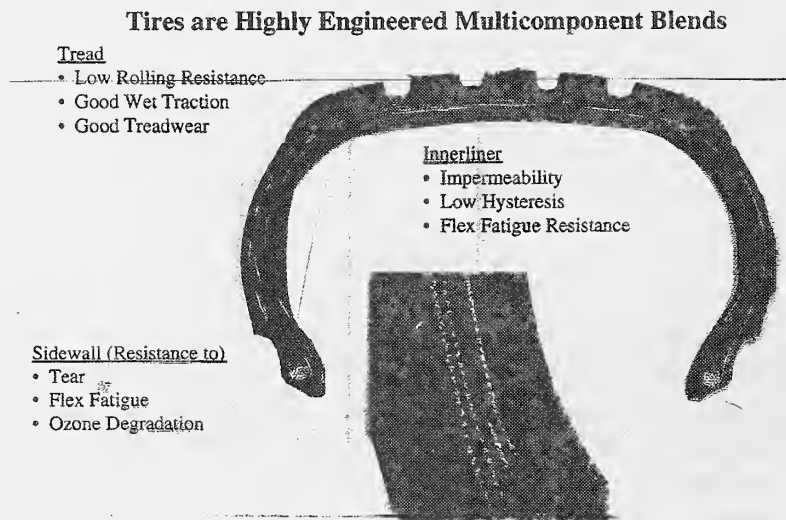**Tires are Highly Engineered Multicomponent Blends**

Tread
• Low Rolling Resistance
• Good Wet Traction
• Good Treadwear

Innerliner
• Impermeability
• Low Hysteresis
• Flex Fatigue Resistance

Sidewall (Resistance to)
• Tear
• Flex Fatigue
• Ozone Degradation

Fig. 1

Predictable Vulcanization and Performance for Elastomers

Polymer Type
Filler Type and Content
Curative Type and Content

Vulcanizate Properties
Crosslink Density & Distribution
Filler Distribution & Polymer Interaction
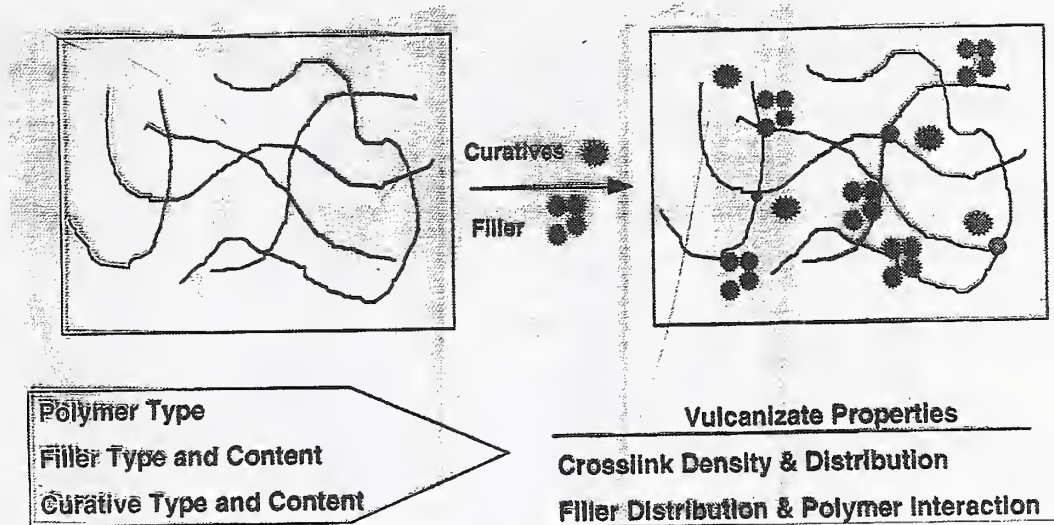
Fig. 2

Vulcanization of an Elastomer Blend

Polymer Composition Volume Fraction	Phase Size and Structure	Microscopy Scattering
Filler Type Volume Fraction	Interaction with polymer Distribution within and between polymer phases	NMR Adsorption Microscopy
Crosslink Density	Distribution within and between polymer phases	NMR Mechanical analysis Swell/DSC
Curative Type	Distribution within and between polymer phases	Microscopy ToF-SIMS

Fig. 3

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Competitive Adsorption to Silica

Polymers	time of coadsorption (hr)	Composition by MAS-NMR*	weight percent carbon
BR; BIMS	1	≥ 95% BR	4.81
	66	≥ 95% BR	5.17
SBR; BIMS	1	≥ 95% SBR	6.34
	66	≥ 95% SBR	6.49
PS; BIMS	1	> 95% PS	22.36
	144	> 95% PS	23.76
BR; SBR	1.5	> 95% BR	6.37
	96	> 95% BR	7.57
BR; PS	1.5	>95% BR	6.48
	120		6.78
1,4-BR; 1,2-BR	1.5	>95% 1,4-BR	6.48
	120		6.78

BR > SBR ~ 1,2-BR >*IR* > PS > BIMS > IMS

Fig. 4

Diffusion of Chains Inhibited by Surface

- **Neutron Reflectivity**
  - **Chain diffusion slows near an interface**
  - **BIMS - dBR layer interdiffusion studies**
    - **Interdiffusion slows down dramatically in thin (20 nm) films**
    - **Carbon black appears to also inhibit interdiffusion**

Fig. 5

*"**Evolving Structure/Property Relationships for Precipitated Silica**"*, <u>Jo-Ann Bice</u>, PPG Industries, Inc., Monroeville, PA

This talk was focussed on precipitated silicas rather than fumed silicas. The motivation for the studies were that recent studies indicated that silica particles in rubber improved properties of tire-wear resistance and moves forward in the step towards "green" technology. The processing conditions of filled systems dictate final properties, but the final properties are difficult to predict a priori. For these processes, in situ analysis techniques are therefore preferred. Determination of the microporous structure can be done by mercury porosimetry or oil (DBP) absorption. Determination of contact angle is however a more difficult problem. Residual porosity is found to affect the density measurements, and the poor determination of density is a big problem. Precipitated silica surface area can be determined by adsorption techniques, as enumerated by other speakers.

Surface preparation is important, since the chemistry of the surface determines the nature of the interactions with polymers as well as other additives. This is also related to wettability issues. Titration and spectroscopy are not useful in this regard. Other techniques give average values, but are not geometry specific (Same as with the density problem). Impurities are found to have a profound influence on surface chemistry.

Discussion- Any quantitative measure for energy required to disperse filler? (A: Not really).

2.4 Nanocomposites Session

*"**Structure and Dynamics of Polymer Nanocomposites**"*, <u>Emmanuel P. Giannelis</u>, Dept. of Materials Science and Engineering, Cornell University, Ithaca, NY

Composites with dimensions in the range of 1 nm to 100 nm, so-called nanocomposites, are the subject of intense current research and development. In particular, nanocomposites synthesized by intercalation of polymers in layered silicates exhibit many advantages including improved mechanical properties, outstanding diffusional barrier properties as well as flame resistance and self-extinguishing characteristics. The talk reviewed the physical and mechanical properties of nanocomposites and discussed them in terms of their static (neutron scattering and computer simulations) and dynamic (including NMR and dielectric relaxation) properties.

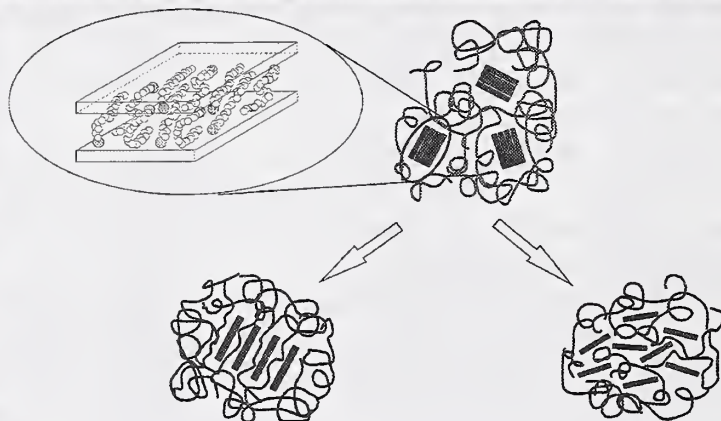*Select Figures (Next Page)*

Nanostructures

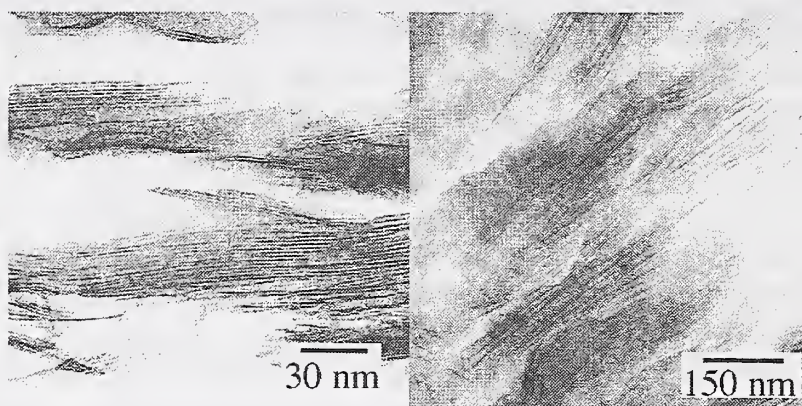# Polymer / Silicate Nanocomposites
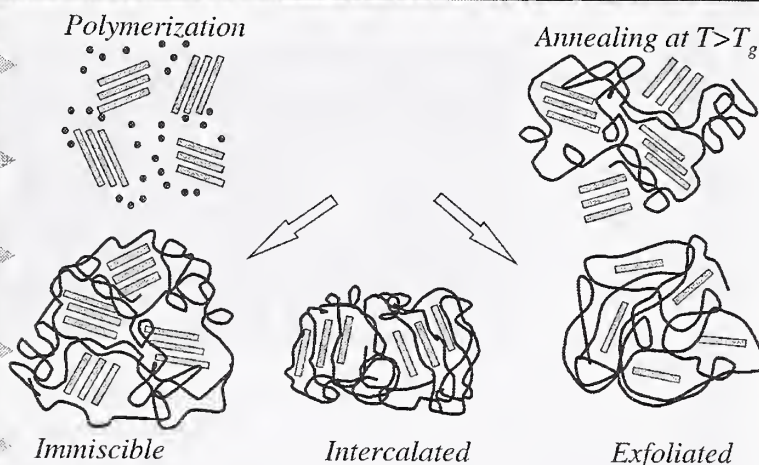# TEM Viewgraphs

30 nm

150 nm

Synthetic Approaches

Polymerization

Annealing at $T>T_g$

Immiscible   *Intercalated*   *Exfoliated*

Fig. 3

Properties of Nylon-6 / Nanocomposites

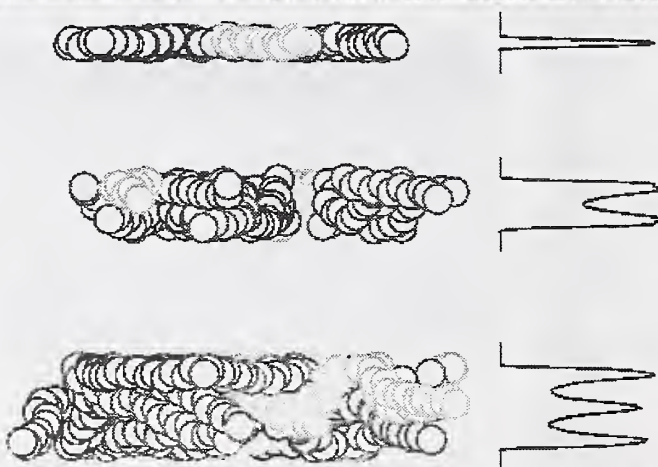| Property	Nanocomposite	Nylon-6
Tensile Modulus (GPa)	2.1	1.1
Tensile Strength (MPa)	107	69
HDT (°C)	145	65
Impact Strength (kJ/m^2)	2.8	2.3
Water Adsorption (%)	0.51	0.87
CTE(x, y)	6.3×10^{-5}	13×10^{-5}

Fig. 4

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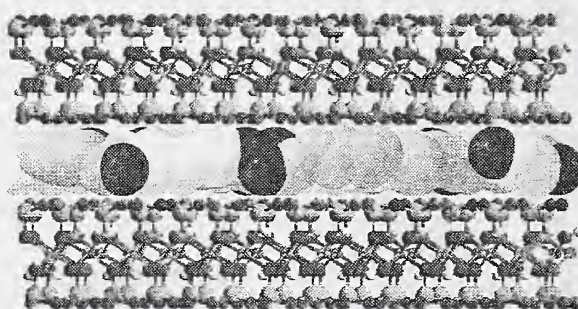
Computer Modeling

Hackett, Manias and Giannelis,
J. Chem. Phys. **108**, 7410 (1998).

Fig. 5

Computer Modeling

J. Chem. Phys. **108**, 7410 (1998)

Fig. 6

*"**Montmorillonite Clay Structures and Intercalation Chemistries Based on Dipole Moment Interactions**"*, <u>Gary Beall</u> and Karl Kamena, Nancore, Inc., Arlington Heights, IL

A new approach to montmorillonite clay surface modification has been developed to compatibilize clays with polymers to prepare nanocomposites. Dr. Beall explained that this new technology was referred to as ion-dipole treatment. The treatment method was described in some detail as well as its implications for nanocomposites. Two issues were discussed that have exhibited significant effects on nanocomposite properties and performance. The first involves the issue of clay purity. Data indicated that clay purity has a strong effect on engineering properties of nanocomposites, especially elongation and impact resistance. The second concerns the effect of clay on permeability. The traditional explanation for the improved barrier of nanocomposites is one of tortuous path. The effect of clay purity level was examined as well as intercalation chemistries that complicate permeability predictions and permanent properties and long term behavior.

*"**Dispersion in a Clay Nanocomposite; Application of Radiation Scattering**"*, <u>Chris D. Muzny</u>, B.D. Butler and H.J.M. Hanley, NIST, Boulder, CO

The potential of using clay as the filler in a polymeric organic/inorganic composite is well understood and appreciated. The properties, however, of the resulting composite are most influenced when the largest possible clay surface area is presented to the polymer matrix. Ideally, then, the clay should be fully dispersed (exfoliated) into its constituents-negatively charged platelets about 1 nm thick and 20 nm to 200 nm in diameter – and bonded to the matrix using an appropriate cationic organic intermediary. Unfortunately, clay platelets tend to form large aggregates in the presence of organics, so they normally will not disperse. A proposed route to prevent clay aggregation by forming platelet-surfactant micelles was presented. The procedure is based on performing a cation exchange reaction between the clay and a surfactant monomer and then adding sufficient excess monomer to give clay-micelle complexes. From chemical analyses of the samples, combined with light and small angle neutron scattering, the estimated excess monomer corresponded to four cation exchange equivalents. In the preliminary work, the complex was then polymerized with acrylamide. Dispersion of the clay was verified by following the synthesis using dynamic light scattering , X-ray scattering, and electron microscopy. It was argued that proof of dispersion is well demonstrated from dynamic light scattering data, thus indicating the potential of the technique of dynamic light scattering as a tool to monitor a synthesis process involving particulates. Problems arising from dispersing a nanometer scale clay mineral in a polymer matrix were discussed.

Some of the issues which needed to be addressed were: 1) Can clay be dispersed in organic solvents? 2) Which is preferred for better properties - homogeneous dispersion or delamination? 3) How can clay content be increased in solvent? 4) How to prove covalent bonding to the surface of the clay occurs? 5) Is crosslinking important? Discussion- Crosslinking is important for compressive strength in composites, therefore, it is probably an important issue here.

"Nanocomposites from Polymers and Layered Minerals", <u>Leon H. Gielgens</u>, H. R. Fischer, T. P. M. Koster, Tno-Tpd Institute of Applied Physics, Materials Division, P.O. Box 595, 5600 AN Eindhoven, The Netherlands

In his talk, Dr. Gilgens discussed block copolymer modified clays. He introduced nanocomposite materials as consisting of polymeric matrix materials and natural or synthetic layered minerals like clays prepared by using special compatibilizing agents between the two intrinsically non-miscible materials. In their approach, these compatibilizers were block- or graft copolymers, with the idea of combining one part of the polymer identically and/or completely miscible with the organic polymer (matrix compound) and another part compatible/miscible with the natural mineral. The interaction between the first part of the compatibiliser is preferentially an ionic interaction or an interaction via H-bonds. This interaction leads to a separation of the mineral into single sheets and a subsequent homogeneous incorporation of these sheets into the polymer matrix material. The aim of the investigation was to provide a general process for the manufacturing of nanocomposite materials consisting of polymeric matrix materials and homogeneously dispersed layered crystalline inorganic materials. He stated needs in mechanical property evaluation, diffusion data, chemical resistance, high temperature behavior and needs in cost and safety evaluation.

Discussion- Comments include emphasis on cost and the balance between increased modulus but decreased toughness. Suggestion that traditional rubber toughening methods should be successful in these systems to improve brittleness and that complete exfoliation is not always needed.
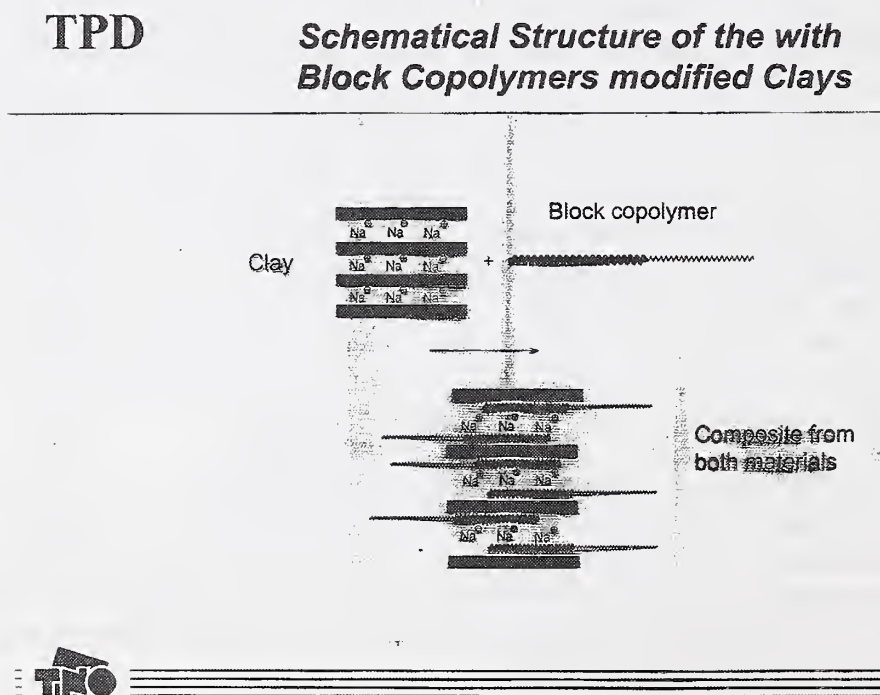
Select Figures

Fig. 1

Clay Nanocomposites - general concept

block copolymer

clay layers

clay compatible block   matrix compatible block

exfoliated clay layers
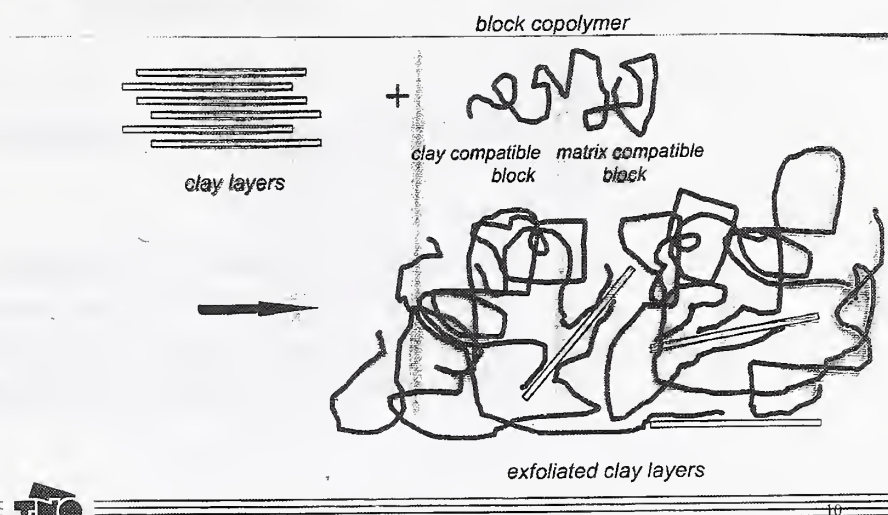
Fig. 2

TPD   *Structure of the Block Copolymers used for the Modification of the Clays*

PEO-PS

P2VP-PS

PEO-PMMA

PMAA-PMMA

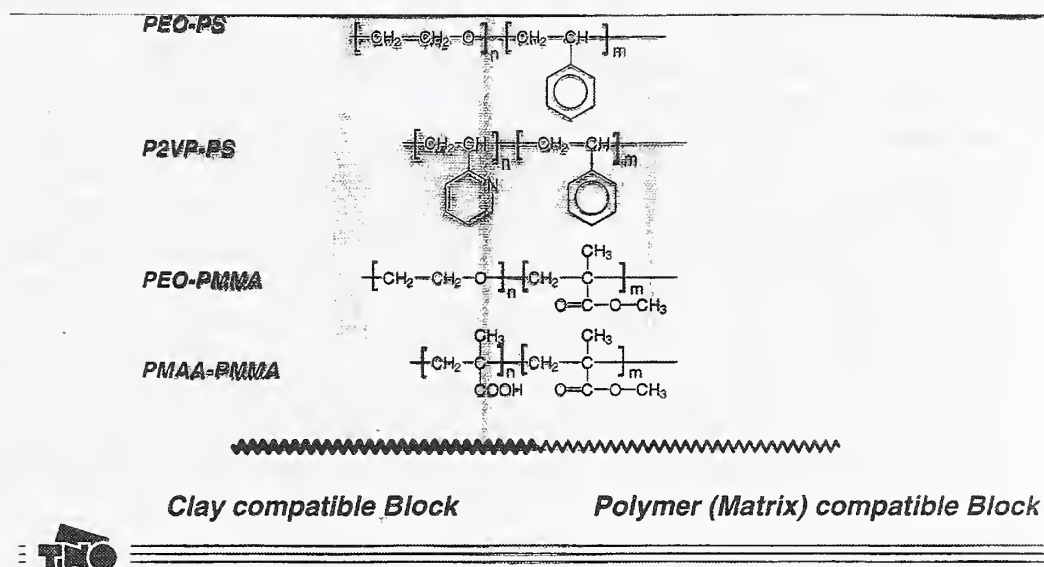*Clay compatible Block*   *Polymer (Matrix) compatible Block*

Fig. 3

35

- *General Concept of Block Copolymers Works*

- *Complete Exfoliation Not Always Needed*
  Good adhesion/interaction between small stacks of
  sheets of the nano-particles and the matrix also supplies
  enhancement of mechanical and thermal properties.

Fig. 4

"Rheological Study of Macro- and Nano- Composites", Ramanan Krishnamoorti, University of Houston, TX

    Dr. Krishnamoorti reported on the rheological behavior of composite materials containing filler particles that led to macro and nanocomposites. The rheological properties of intercalated and exfoliated nanocomposites of a homopolymer were examined using oscillatory shear and the terminal regime flow characteristics were found to be distinctly different – the exfoliated nanocomposites exhibited liquid like behavior while the intercalated nanocomposites exhibited characteristics intermediate between a liquid and a solid. Dr. Krishnamoorti also reported on the linear viscoelastic, alignment characteristics and non-linear oscillatory shear behavior of an end-tethered nanocomposite. These were shown to be model melt-brush systems and exhibited extraordinary strain hardening characteristics. Finally, Dr. Krishnamoorti reported on structural and viscoelastic characteristics of a block copolymer based nanocomposite. The rheological properties in the terminal regime were found to be pseudo-solid like and consistent with the response from a "hairy-disc" object.

Select Figures (Next Page)
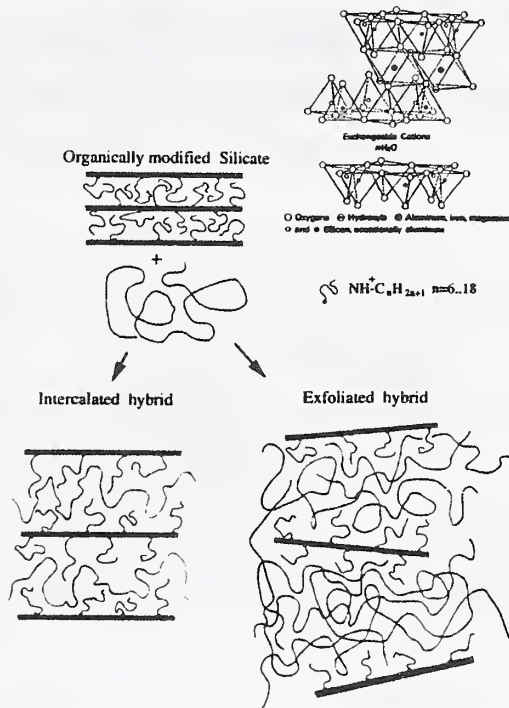
Polymer - Layered Silicate Nanocomposites

Organically modified Silicate

O Oxygen ⊘ Hydroxyls ⊛ Aluminum, iron, magnesium
○ and ● Silicon, occasionally aluminum

Exchangeable Cations
nH₂O

$NH^{+}-C_nH_{2n+1}$ n=6..18

Intercalated hybrid   Exfoliated hybrid

Fig. 1

- ● Nanocomposites
    - » Intercalated
    - » Exfoliated
    - » End-Tethered
    - » Structured Polymers

- ● Macrocomposites
    - » Carbon Black + BIMS

Fig. 2

Melt Rheology

Dynamic Oscillatory Shear

Transducer

25 mm Parallel Plates with Polymer Sample

Temperature Controlled Oven

Polymer Sample

Motor
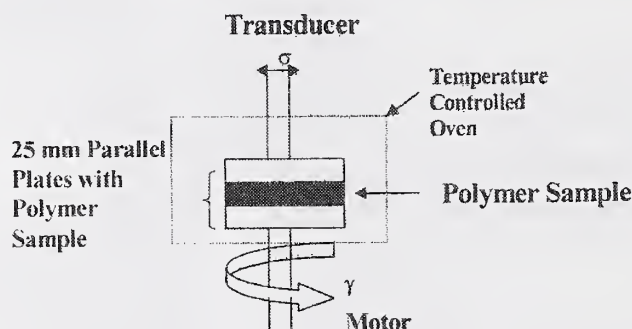
Fig. 3

Apply

Measure

$$\gamma = \gamma_0 \sin(\omega t) \qquad \sigma = \gamma_0 (G' \sin(\omega t) + G'' \cos(\omega t))$$

- Melt State Rheology suggests a Correlation Between Flow Properties and Interaction Strength.
- Templating Nature of Silicate Layers.
- End-Grafted Nanocomposites similar to Polymer Brushes

Fig. 4

"Flammability Studies of Polymer Layered Silicate Nanocomposites", Jeffrey W. Gilman, Takashi Kashiwagi, Sergei Lomakin[†], National Institute of Standards and Technology, Gaithersburg, MD; Emmanuel P. Giannelis, Evangelos Manias Cornell University, Ithaca, NY; [†] Guest Researcher at NIST from the Russian Academy of Sciences, Moscow, Russia.

Dr. Gilman reported on the enhanced thermal properties and improved flammability properties of polymer-layered silicate (clay) nanocomposites. He showed that both delaminated and intercalated nanostructures have improved flammability properties. His collaborative research program with Dr. Giannelis at Cornell University has focused on demonstrating the generality of the flammability behavior and on studing the mechanism of the flame retardant effect of the nano-dispersed clay. XRD and TEM analysis was used to identify a nano-reinforced silicate/carbon-like char from the combustion residue. Dr. Gilman felt the presence of this high-performance char supports a physical rather than a chemical mechanism of flammability control. A NIST-Inductry Consortium has been formed to further study the flammability properties of nanocomposites.

Presentation Outline

‾1. Background

2. PA-6 clay Nanocomposites
    a) Synthesis, structure and properties
    b) Flammability properties

3. Intercalated clay Nanocomposites
    a) Thermoplastics
    b) Thermosets

4. Radiative Gasification

Fig. 1

Fire Retarded Polymers by Enhanced Char Formation

- Increased char yield
- Increased rate of char formation
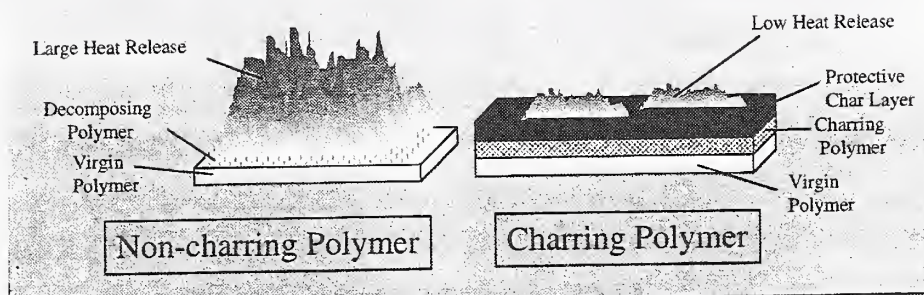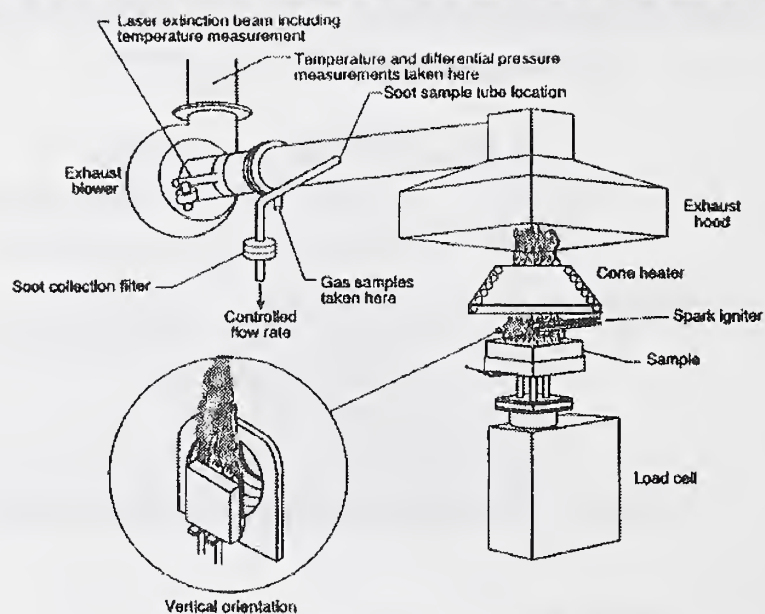- Lower density char
- $T_{Process} \ll T_{Charring} \sim T_{Decomp}$

Fig. 2

A schematic view of the cone calorimeter.

Scenario	Time to incapacitation (s)	Time to death (s)
Base case	180	>600
Double heat release rate	160	180
Double material toxicity	180	>600
Halve ignition delay	140	>600

Products	Test no.	Fire hazard condition		Predictive variable	
		Total toxicity, expressed as (CO-equiv. kg)	Time to reach untenable conditions in burn room (s)	CO yield (kg/kg)	Peak heat release rate (kW)
non-FR	N1	21	110	0·22	1 590
non-FR	NX0	17	112	0·18	1 540
non-FR	NX1	16	116	0·14	1 790
FR	F1	2·6	∞	0·22	220
FR	FX0	5·5	1 939	0·23	370
FR	FX1	6·1	2 288	0·23	350
FR	FX1a	5·6	1 140	0·23	450

Vytenis Babrauskas, Richard D. Peacock

Fig. 3

40

Inorganic Materials as New Flame Retardants

Polycarbosilane PCS

Polysilastyrene PSS

Silsesquioxane
R = Me, Ph (1:1)

Preceramic Blends and Grafts

Low melting Glasses

ZrO_2 in Borate salts

Silica Gels

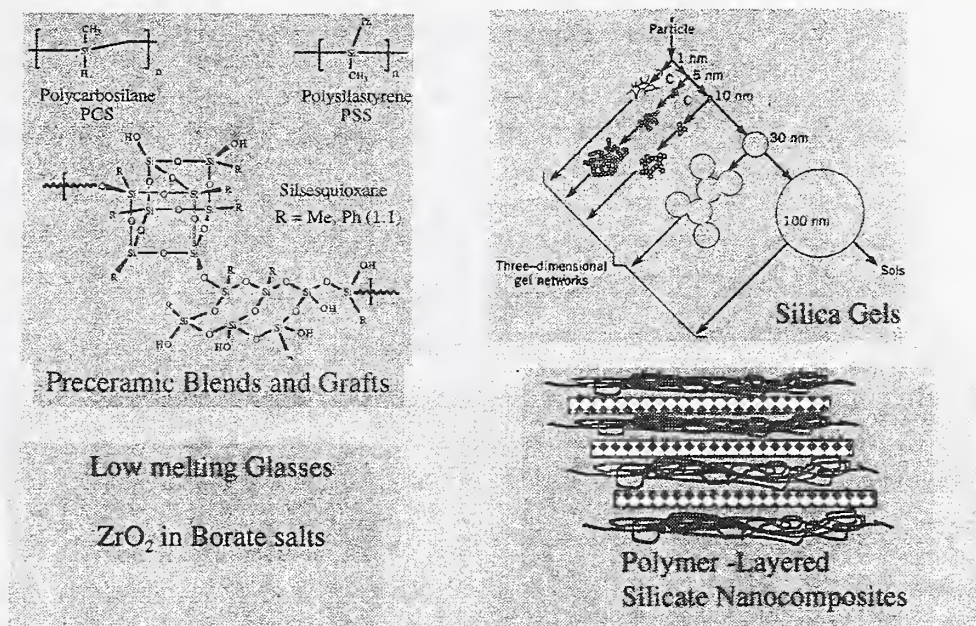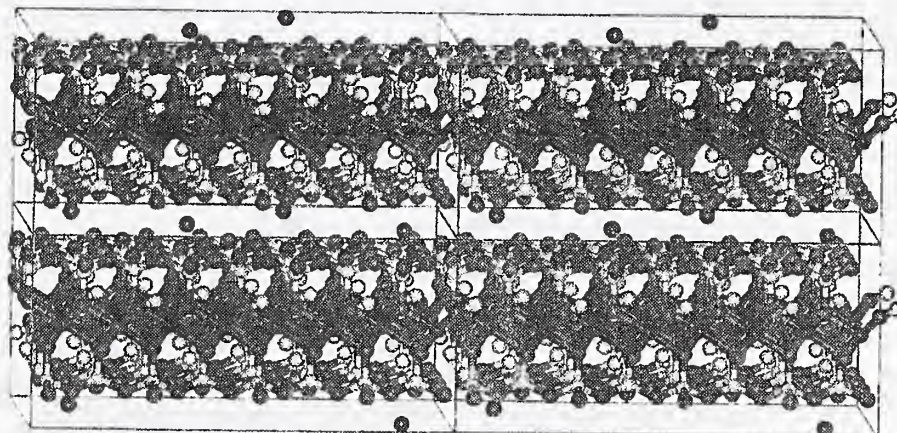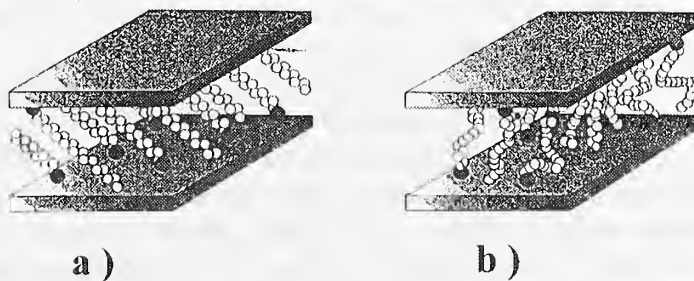Polymer -Layered
Silicate Nanocomposites

Fig. 4

Na+ Montmorillonite Structure

18 *Chem. Mater., Vol. 6, No. 7, 1994*

Vaia et al.

a)

b)

Nyden (NIST), Gianellis, Manias (Cornell)

Fig. 5

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• The HRRs of thermoplastic and thermoset polymer layered silicate nanocomposites are reduced by 40 % to 60% in delaminated or intercalated nanocomposites containing a silicate mass fraction of only 2 % to 6 %. Furthermore, this system does not increase the carbon monoxide or soot produced during the combustion.

• Not only is this a very promising new method for flame retarding polymers, but it does not have the usual drawbacks associated with other additives. That is, the physical properties are not degraded by the additive (silicate); instead they are improved..

• The nanocomposite structure of the char appears to enhance the performance of the char layer. This layer may act as an insulator and a mass transport barrier slowing the escape of the volatile products generated as the polymer decomposes.

Fig. 6

"Dynamics of polymers in confined geometries: Neutron studies of intercalated polymer-clay nanocomposites", <u>Robert Ivkov</u>, A. Karim, E. Amis, N. Malizsewskyi, P. Gehring, NIST; R. Krishnamoorti, Dept. of Chemical Engineering, Univ. of Houston, Houston, TX

Dr. Ivkov discussed the use of neutron scattering methods to characterize the structure and dynamics of polymers such as polyethylene oxide (PEO) intercalated into fluorohectorite clay. He described the filter-analyzer spectroscopy technique to characterize the high energy dynamical features, and neutron time-of-flight and spin-echo spectroscopy to characterize the low energy, larger spatial features of these materials. Intercalated materials were prepared by melt intercalation of 100,000 M_w polyethylene oxide (PEO) into fluorohectorite (FH) clay. Several samples were made with varying amounts of polymer mass fraction, 18 %, 25 %, and 30 %. The extent of intercalation was characterized by x-ray diffraction, and all samples were stored in a dessicator under vacuum until use. The samples were loaded into aluminum sample holders sealed with indium wire in an inert (dry He) atmosphere in a glove box immediately before use.

Neutron filter-analyzer spectra were obtained at a temperature of 10 K for all samples described above, and were compared with those obtained from bulk PEO and pure clay. The data reveal only subtle differences among the intercalated materials and the bulk PEO, suggesting that the vibrational motions of the hydrogens in the polymer do not experience a significantly different environment upon intercalation. Neutron time-of-flight data taken at 20 K below the glass transition of PEO (213 K) reveal significant differences between the intercalated materials and the bulk polymer. Bulk PEO displays several peaks that result from vibrational modes of the crystalline regions of the polymer. These features diminish with intercalation. Another prominent feature observed in the bulk PEO is the low energy plateau (-2 meV to -8 meV) common to the glassy state. With 30 % intercalation, the plateau becomes a shoulder and almost completely disappears in the 18 % PEO sample, suggesting that the intercalated polymer chains are not in the glassy state.

Discussion-Comment that extension of studies to examine slower molecular motion modes might be enlightening for fatigue and failure studies and long term stability of filled polymers.
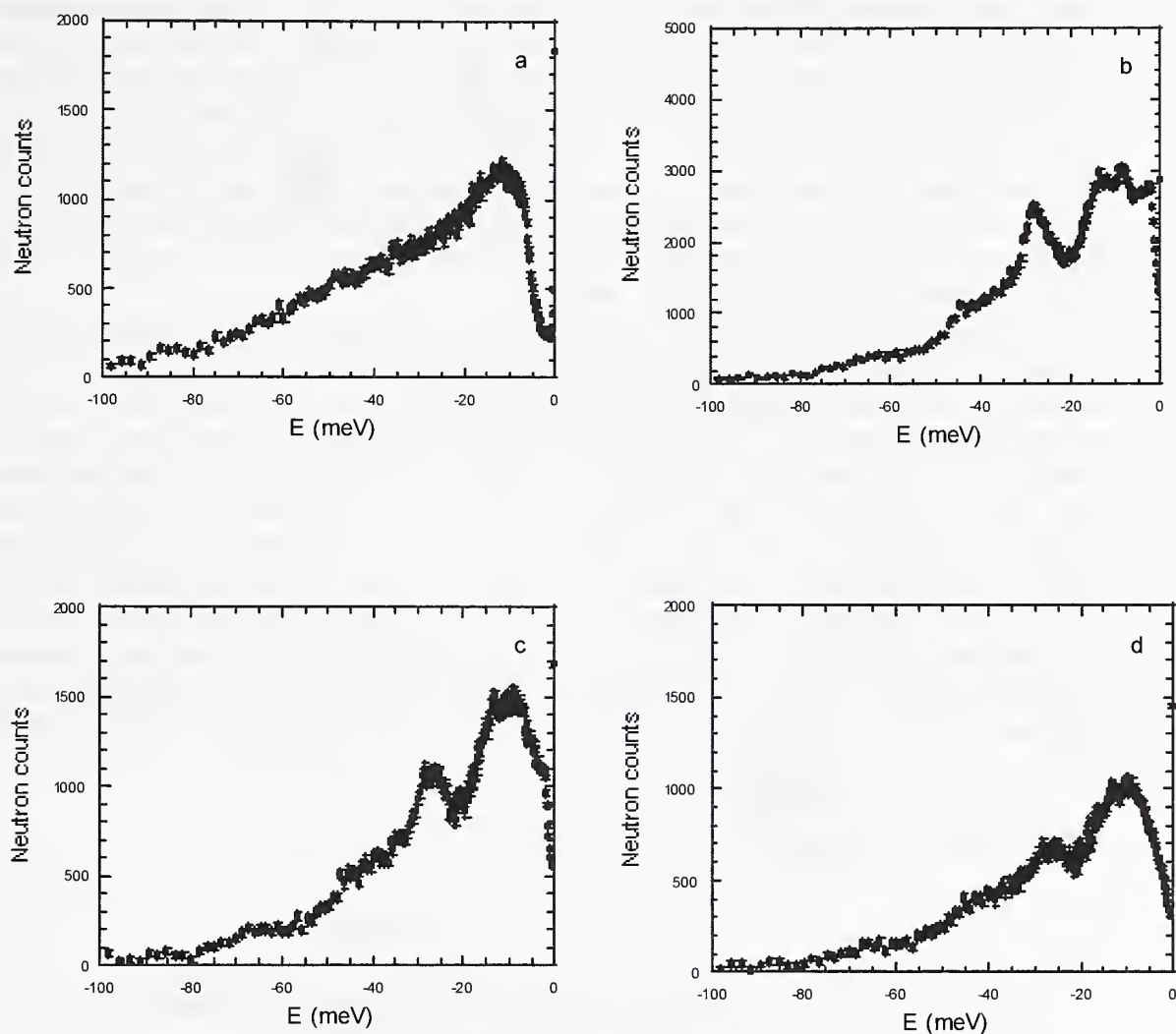
Select Figures

Fig. 1: Plots of neutron time-of-flight data obtained from samples at 193 K (20 K below the glass transition of bulk PEO) : a) pure fluorohectorite clay, b) pure polythylene oxide (PEO); c) 30 % PEO intercalated with fluorohectorite clay, and d) 18 % PEO intercalated with fluorohectorite clay. These reveal significant differences between intercalated materials and bulk polymer. Several features seen in bulk PEO get suppressed with intercalation. Together, the results suggest that intercalation of PEO into clay galleries significantly reduces interchain interactions to the point that the chains no longer retain their macroscopic properties.

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2.5 Theory and Modeling Session

"Effect of fillers and their distribution on composite properties," C.K. Hari Dharan, Dept. of Mechanical Engineering, University of California, Berkeley, CA

Dr. Dharan stated the needs for gathering knowledge of local properties of the filler, elastic yield properties, interface strength, friction coefficients, and in-situ properties. Using homogenization techniques, certain effective properties of polymer composites can be derived from the volume fraction, distribution and properties of the reinforcing phase. Such approaches are useful for "designing" the composite so that desired properties can be obtained at desired locations. For these approaches to be useful, however, one needs to take a systems view, particularly a knowledge of the overall requirements of the structure. Thus, while so-called micromechanics approaches are used to homogenize the composite, the utility of the material depends upon component and application constraints which must be specified, requiring the materials designer to be cognizant of the application before the material can be designed.

This approach is illustrated by investigating the problem of an axisymmetric body subjected to thermal gradients. The desired distribution and properties of the reinforcement phase to minimize thermal stresses are obtained through the use of a homogenization scheme. Effective inhomogeneous material properties are obtained through the use of distribution functions that relate the concentration of the second phase with the coordinates of the structure. Using these properties, inhomogeneous eigenstrained media analyses are conducted for such axisymmetric bodies, and in this fashion, the desired shape and material properties of the reinforcement phase, and its close-optimal distribution, are determined. A similar approach was outlined for the case of a structure subjected to both internal and external pressure and to thermal gradients. Discussion- Areas requiring additional research, particularly the characterization of interfaces and in-situ properties in polymer composites, such as with a tensile stage for TEM.

Select Figures

Approach

- **Derive "local" effective properties using homogenization techniques**
- **Define distribution functions for filler**
- **Determine performance parameters (stress, CTE, conductivity, transmission loss, etc.) for each specific application**
- **For yielding, fracture, and slip, we must resort to numerical techniques**
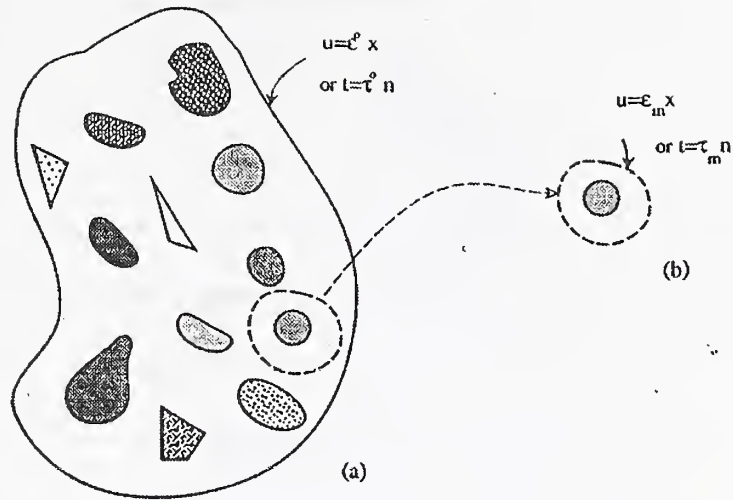
Fig.1

Figure 1(a): Schematic of a general composite material:
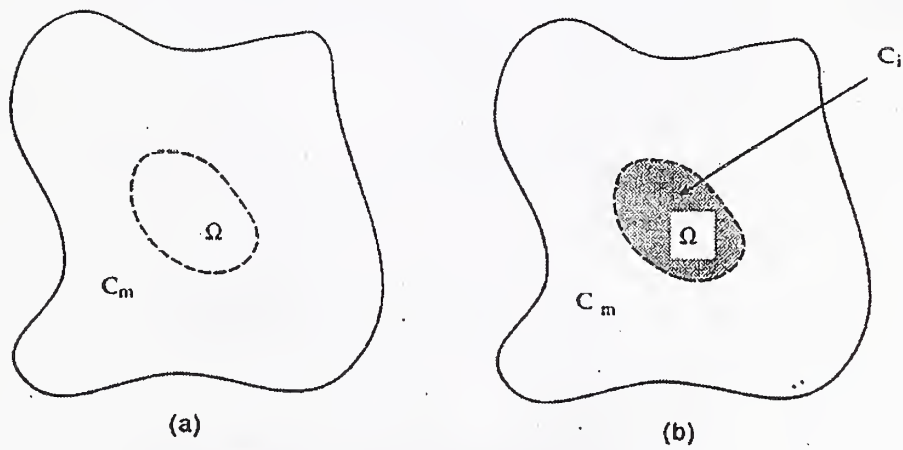Figure 1(b): A single inclusion surrounded by the matrix phase

Figure 2: Eshelby's equivalent inclusion method

Fig. 2

Effective Stiffness Tensor

$$C_{eff} = C_m + v\,(C_i - C_m)\,A_i$$

Where

$$A_i = T\,[\,(1 - v)\,I + vT\,]^{-1}$$

$$T = [\,I + E\,S_m\,(C_i - C_m)\,]^{-1}$$

C_m = Matrix Stiffness Tensor

S_m = Matrix Compliance

C_i = Inclusion Stiffness

v = Volume Fraction

E = Eshelby Tensor (See Mura, 1987)

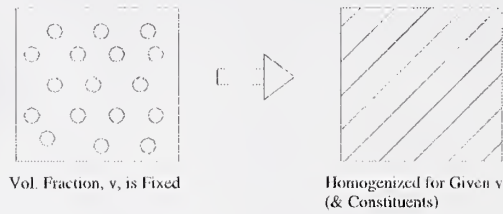## CTE (Coefficient of Thermal Expansion)

$$\alpha_{eff} = \alpha_m + (\alpha_i - \alpha_m)\,B_i$$

Where

$$B_i = (S_i - S_m)^{-1}\,(S_{eff} - S_m)$$

Fig. 3

Vol. Fraction, v, is Fixed   Homogenized for Given v (& Constituents)

However

In composites, we (ought to) have the ability to tailor properties to meet requirements at different locations.
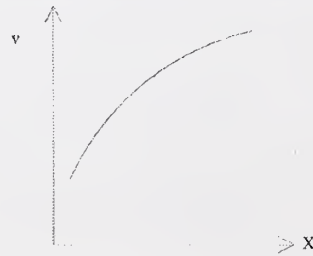
Fig. 4

1. Tube with internal
   & external pressure
   & heat flux
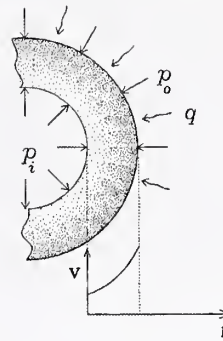
2. Beam under bending
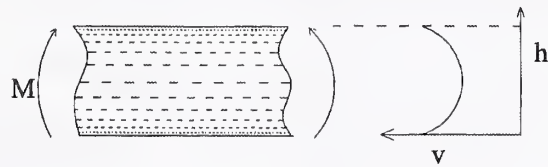
Fig. 5

3. Tube under torsion

Maximize torque
capacity

4. Bearing surface

(Articular cartilage)

(Porous hydrophillic
elastic reservoir)

Piston
Pin

Fig. 6

47
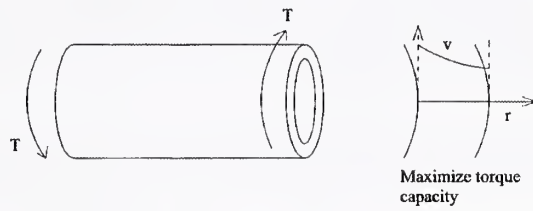
5. Combine fuctions

Fig. 7

What is needed

- **Knowledge of local properties**
  - Filler elastic and yield properties
  - Interface strength, friction coefficient
  - Matrix and interphase *in-situ* properties
- **Define high potential applications/processes**
- **Multi-disciplinary research teaming**

  -Polymer synthesis chemist, physical chemist, physical modeling, experimental models, instrumentation

Fig. 8

"*Model for dispersion rheology*", <u>Jozef Bicerano</u>[1], Jack F. Douglas[2] and Douglas A. Brune[1]; [1]Dow Chemicals, Midland, MI; [2] Polymers Division, NIST, Gaithersburg, MD

A simple quantitative predictive model was developed for the shear viscosity η of dispersions of solids in liquids. The model is based on the fundamental physical concepts of universality and scaling. It does not involve empiricism; that is, calculations using the model do not require any pre-existing data for η(dispersion), either for calibration, interpolation, or for extrapolation. Th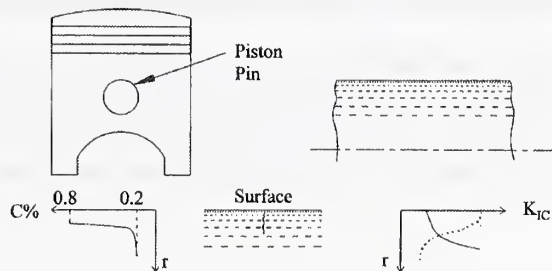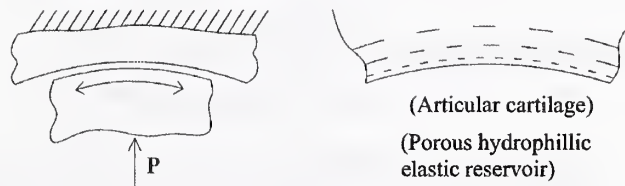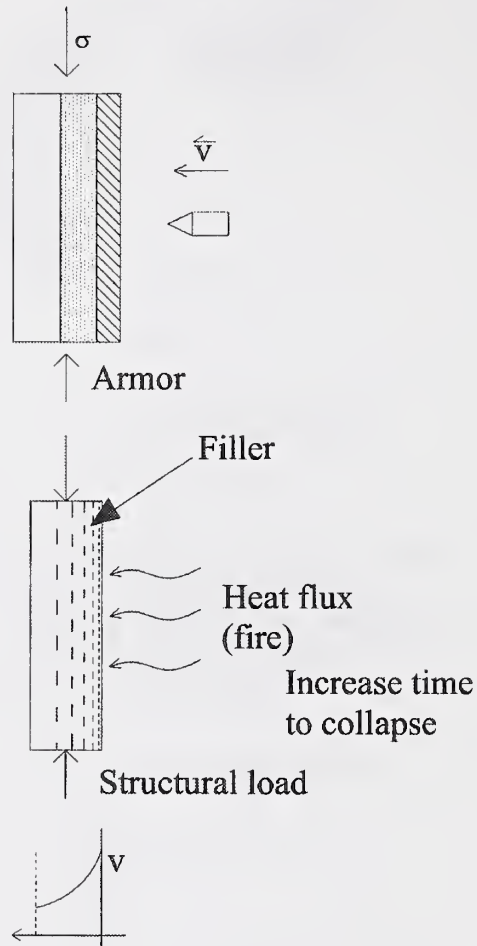e model allows the calculation of η(dispersion) as a function of particle volume fraction, shape, polydispersity, fractal aggregation and flexibility, dispersing fluid viscosity, and shear rate and temperature.

Select Figures

OUTLINE

- **Dilute regime (intrinsic viscosity [η] *versus* particle shape).**

- **Full volume fraction Φ range (η).**

- **Percolation threshold p_c *versus* particle shape.**

- **Maximum packing fraction Φ_m as key parameter.**
  - Effects of particle shape for monodisperse rigid solid particles.
  - Shear rate (SR), absolute temperature (T), and flocculation effects.

- **Examples of viscosity calculations as a function of:**
  - Particle shape.
  - Shear rate (SR).
  - Absolute temperature (T).
  - Viscosity of dispersing fluid.
  - Number of particles (N) and fractal dimensionality (d) of aggregates in flocculated systems.

- **When one finds a finite yield stress (with example).**

- **Polydispersity, flexibility, and "slip" or "plasticization" effects.**

- **Comparison with experimental data of Krishnamoorti *et al*.**

Fig. 1
- **Summary and conclusions.**

A_f DEPENDENCE OF [η]

- Isotropic average of [η] for biaxially symmetric ellipsoids.
- A_f=(length of major axis c)/(length of minor axes a=b).
- A_f>1 for fibers, A_f=1 for spheres, A_f<1 for platelets.
- Squares indicate exact solutions of constitutive equations.
- The curve represents a fitting equation:

$$[\eta] \approx \frac{1012 + 2904A_f - 1855A_f^{1.5} + 1604A_f^{2} + 80.44A_f^{3}}{1497A_f + A_f^{2}}$$
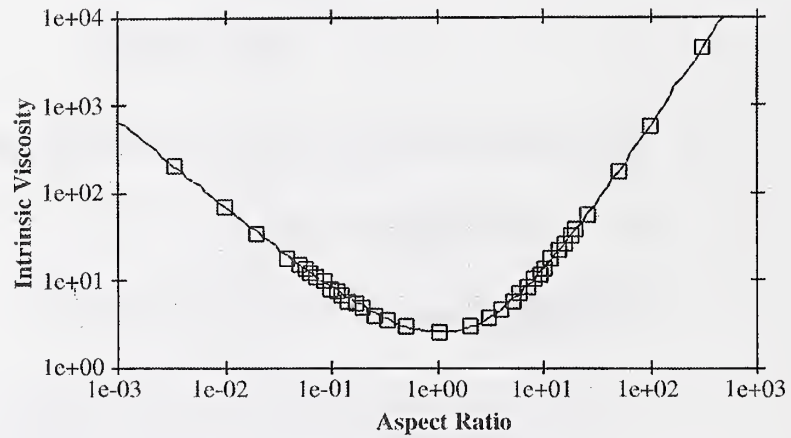
Fig. 2

A_f, SHEAR RATE AND T DEPENDENCE OF [η]

A_f affects [η] at all SR values, while SR and T dependences may occur for nonzero SR via dependence of [η] on Pe.

Fig. 3

50
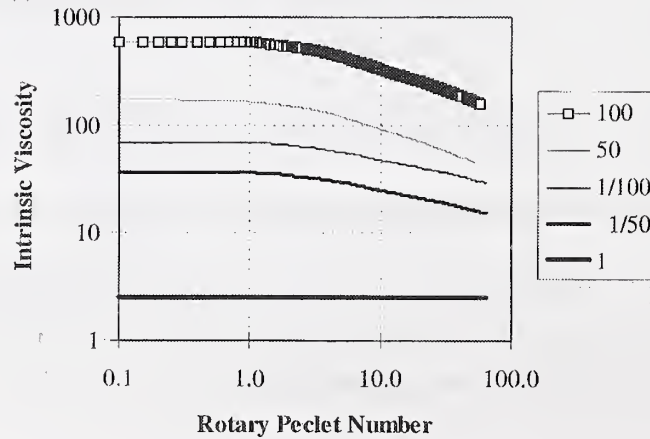
"UNIVERSAL" EXPRESSION FOR η(relative)

- **Dilute dispersion described by a "virial expansion":**

$$\eta(\text{relative}) \equiv \frac{\eta(\text{dispersion})}{\eta(\text{dispersing fluid})} \approx 1 + [\eta]\Phi + k_H \cdot \Phi^2 + \dots$$

- **Concentrated dispersion described by the Maron-Pierce equation (a good semi-empirical expression), where k~1.**

$$\eta(\text{relative}) \approx k \cdot \left(1 - \frac{\Phi}{\Phi_m}\right)^{-2}$$

- **Our new "universal" expression is valid over full range of Φ values, and goes to following limits:**
  - Second-order virial expansion in dilute regime.
  - Maron-Pierce equation with k=0.94 in concentrated regime.

$$\eta(\text{relative}) \approx \left(1 - \frac{\Phi}{\Phi_m}\right)^{-2} \cdot \left[1 - 0.4 \cdot \frac{\Phi}{\Phi_m} + 0.34 \cdot \left(\frac{\Phi}{\Phi_m}\right)^2\right]$$

Fig. 4

"UNIVERSAL" η EXPRESSION *VERSUS* DATA

- **Representative data from work of de Kruif *et al.*, for sterically stabilized hard silica spheres in cyclohexane.**

- **Also good agreement with data from many other sources, for particles of different shapes in different types of fluids.**

Fig. 5

51

52
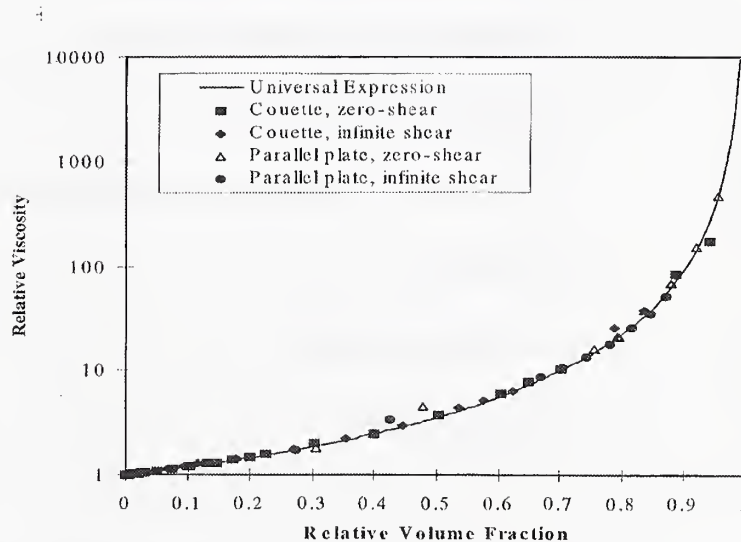
A_f DEPENDENCE OF p_c

- Isotropically placed biaxially symmetric ellipsoids.
- A_f=(length of major axis c)/(length of minor axes a=b).
- A_f>1 for fibers, A_f=1 for spheres, A_f<1 for platelets.
- Squares indicate results of Monte Carlo simulations.
- The curve represents a fitting equation:

$$p_c \approx \frac{9.875A_f + A_f{}^2}{7.742 + 14.61A_f + 12.33A_f{}^{1.5} + 1.763A_f{}^2 + 1.658A_f{}^3}$$
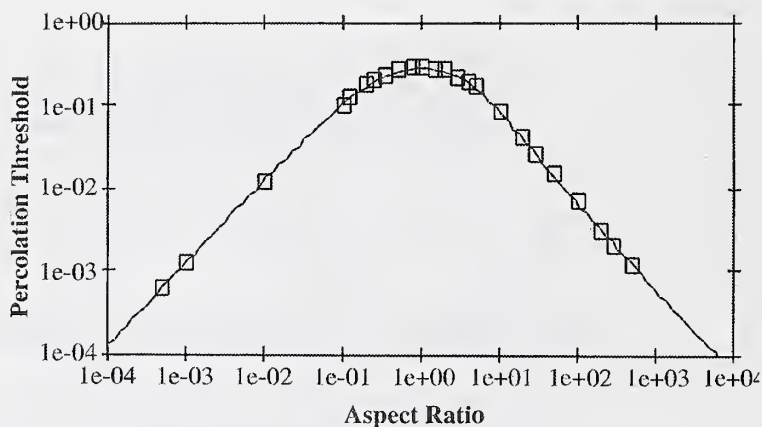
Fig. 6

- A quantitative predictive model was developed for dispersion shear viscosity relative to dispersing fluid, as a function of:

  - Volume fraction of dispersed particles.

  - Shape of dispersed particles.

  - Flocculation (size and fractal dimensionality of aggregates).

  - Shear rate.

  - Absolute temperature.

  - Particle flexibility.

- A computer program and a major manuscript were prepared.

Fig. 7

*"**Modeling the Behavior of Polymer/Clay Nanocomposites**"*, <u>Anna C. Balazs</u>, Chemical Engineering Department, University of Pittsburgh, PA

Dr. Balazs discussed the paucity of knowledge regarding thermodynamic properties of polymer/clay nanocomposites. It is well known that polymer-clay nanocomposites exhibit dramatic increases in tensile strength, heat resistance, and barrier properties as compared to the pure polymer matrix. Insights into these phenomena, and a better understanding of the properties of polymer/clay nanocomposites may by obtained by modeling their thermodynamics. By deriving the free energy for the system, phase diagrams for polymer/clay and polymer/solvent/clay mixtures were constructed. Dr. Balazs's results provided guidelines for fabricating thermodynamically stable nanocomposites with the desired morphology. Dr. Balazs also focussed on the interactions between surfactant-modified clay surfaces and a polymer melt. Using self-consistent field calculations, the various characteristics of the surfactants, polymers and clay surfaces were varied. From the calculations, the optimal conditions for promoting the penetration of the polymer between the organically-modified interfaces were isolated.

ATTENDEES RESPONSE

Surveys were conducted by brainstorming all research and technical needs in the area of fillers and nanocomposites and then ranking the needs by a voting scheme.

3.1 Results of Survey

Rank	Compounding, Reinforcement and Toughening - Research Needs	Score
1	Polymer/Filler Interactions	16
2	Dynamics at Filler/Polymer Interface	15
3	Surface chemistry of fillers (and silane coupling agents)	10
4	Inter"phase" morphology	6
5	What initiates fatigue? Where does it happen?	6
6	Polymer blend thermodynamics in the presence of fillers	5
7	Ideal Systems (e.g. bound versus excluded)	4
8	Correlation between size scale and performance	3
9	Durability and Heterogeneity	3
10	Viscoelasticity measurements of filled polymers - bound fraction from high shear.	3
11	Evolution of morphology related to stiffness/toughness	2
12	Polymer/Filler Networks	2
13	Equilibrium or non-equilibrium? How far away? Timescales.	2
14	Role of crosslinking	2
15	Role of fillers in crystalization	2
16	Orientation/Aspect Ratio with interface at finite thickness	1
17	Modulus interpretation of AFM data	1
18	Thermal/shear effects	1
19	Selectivity of pigments, flame retardant, etc…	1
20	Filler mobility versus polymer mobility	0
21	Chemistry of coupling agents	0
22	Role of surface roughness	0
23	Migration of additives to interfaces	0

Compounding, Reinforcement and Toughening -
Research Needs (85 responses)

19 %

18 %

26 %

5 %

6 %

7 %

7 %

12 %

Polymer/Filler interactions

Dynamics at polymer/filler interface

Filler surface chemistry

Interphase morphology

Fatigue mechanism

Thermodynamics with fillers

Ideal systems

Other (12 topics)
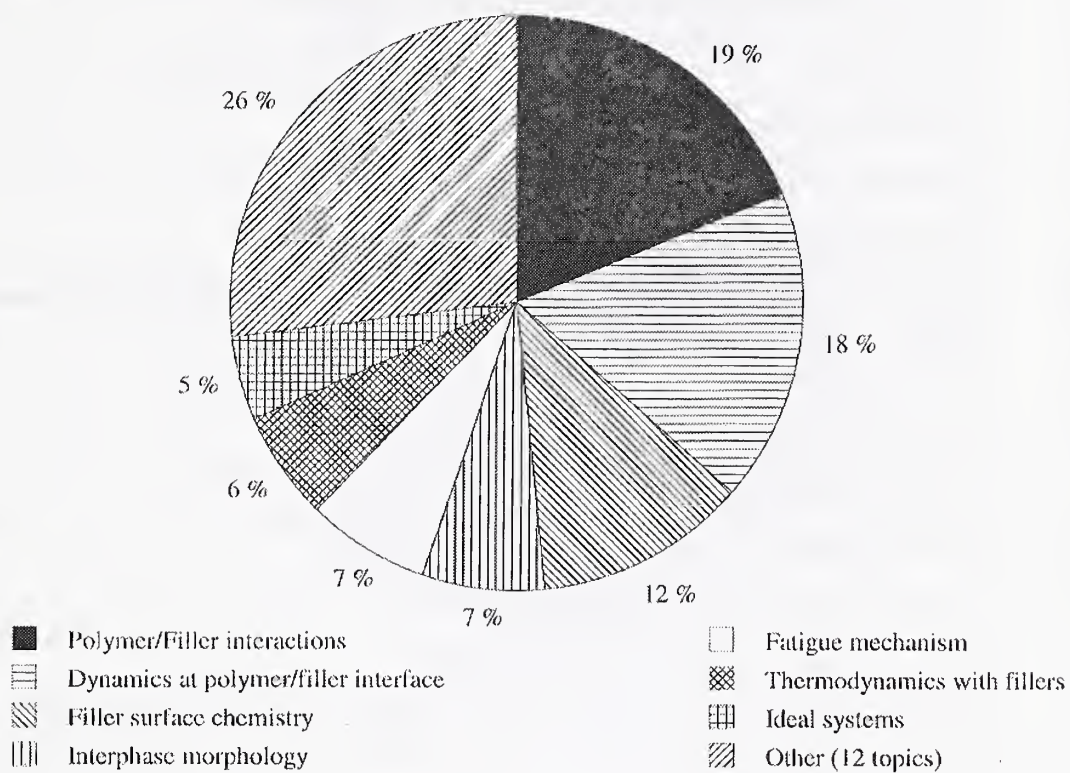
Results of Survey (cont'd)

Rank	Compounding, Reinforcement and Toughening – Technological Needs	Score
1	Measuring transient morphology	10
2	Less expensive/less labor intensive technique for characterizing dispersion	8
3	Online probes of distribution. Process monitoring	7
4	AFM instead of TEM to look at filled systems (10nm resolution)	4
5	Resistivity Measurements/Lumped Impedance	4
6	Mobility at interface in high temperature systems	3
7	Measuring Exchange with Scattering	2
8	New Visualization Techniques for seeing networks. Magnetic Resonance Imaging (MRI)	1
9	Low temperature atomic force microscope (AFM)	1
10	Mechanical-optical	0
11	Online probes of dispersion	0
12	Filler migration	0
13	In-situ nanoscale probe (cheap, portable, etc…)	0
14	How to measure fatigue. Real-time, in-situ	0
15	Measuring small strains at small length scales	0
16	post-processing evolution	0
17	Understanding and eliminating "skin" effects	0
18	High frequency measurements in cured state	0
19	Entanglement with bound fraction	0

**Compounding, Reinforcement and Toughening -
Technological Needs (40 responses)**

17.5 %

25 %

10 %

10 %

20 %

17.5 %

■ Measuring transient morphology	|||	AFM vs. TEM
▤ Easier dispersion characterization	☐	Electrical measurements
▨ Online process monitoring	▩	Other (14 topics)
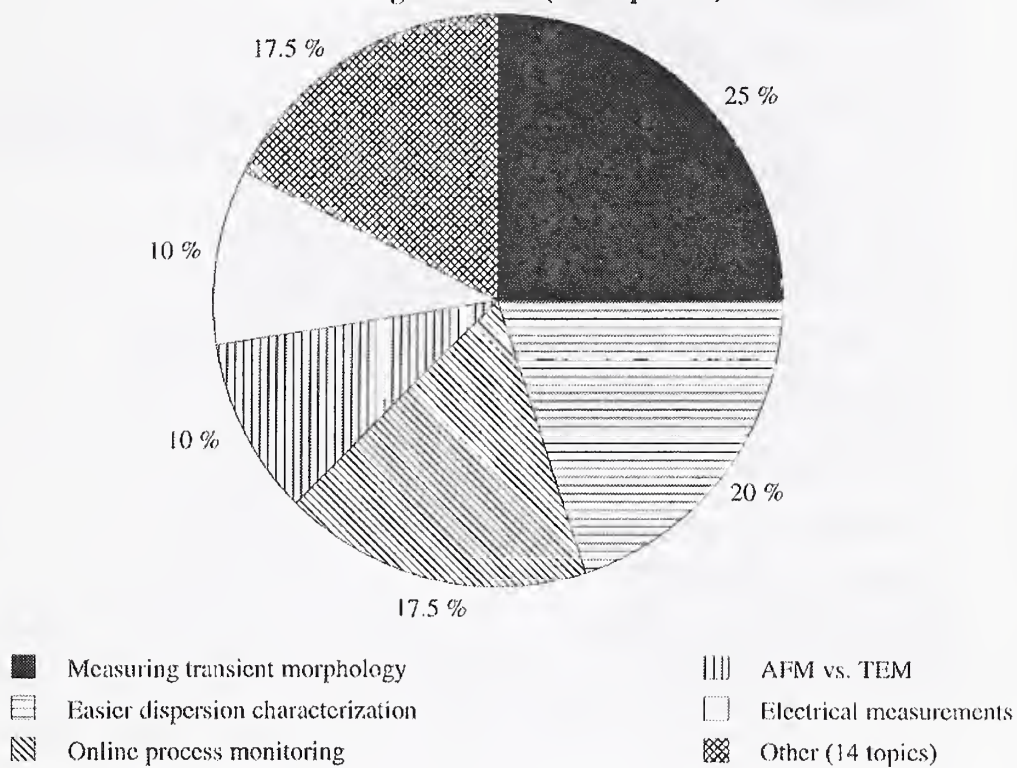
Results of Survey   (cont'd)

Rank	Nanocomposites – Research Needs	Score
1	Structure/dynamics in confined media	8
2	Characterization method for degree of intercalation	4
3	Characterization of thin film mechanics	4
4	exfoliation - mechanism	3
5	dielectric spectroscopy for nanocomposites	3
6	Measure barrier properties/transport	3
7	Define length scales of morphologies relating to known physical properties	2
8	Positron annihilation	2
9	Mechanics of nanocomposites	1
10	Intercalated models based on capillary theories	1
11	Method to monitor/characterize degredation during processing	1
12	Polydispersity on intercalation	0
13	Characterization of interphase layer in semi-crystalline	0
14	Comparison of same volume loading of fillers (e.g. Si, CB)	0
15	NMR for nanocomposities	0
16	SANS for nanocomposites	0
17	Replacement/addition to TEM	0
18	Examine purity issue	0

Nanocomposites - Research Needs (32 responses)

25 %

12.5 %

12.5 %

9 %

9 %

9 %

23 %

Legend:

- ■ Structure/dynamics in confined media
- ▤ Characterization of degree of intercalation
- ▧ Characterization of thin film mechanics
- ▥ Exfoliation mechanism
- ▢ Dielectric spectroscopy
- ▨ Barrier/transport properties
- ▦ Other (12 topics)
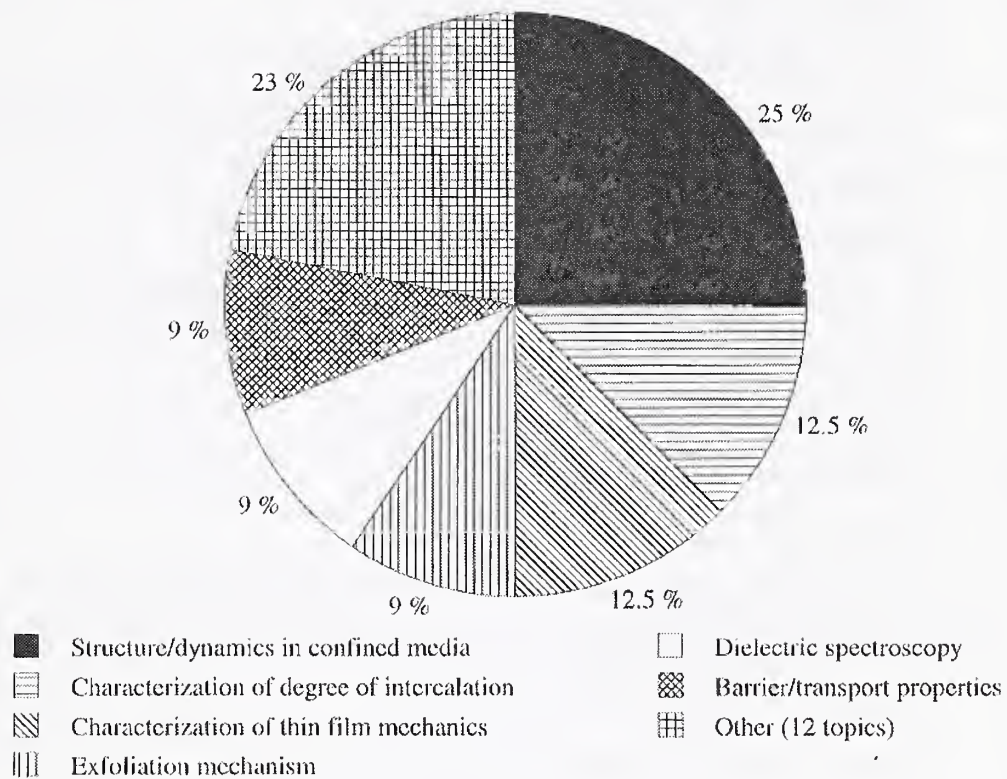
Results of Survey (cont'd)

Rank	Nanocomposites – Technological Needs	Score
1	Characterize degree of exfoliation	6
2	Functionalized AFM tips	4
3	Nanomechanics - real-time measurements of fracture, toughness	4
4	Enthalpy measurements - microcalorimetry	3
5	How to probe dynamics at different time scales?	3
6	Technique that combines global probe (SAXS, XRD) with local (TEM) that is fast	3
7	Standard sampel preparation method for XRD	2
8	Measure anisotropy - dielectric, etc.	2
9	Methods to characterize starting material - different length scales relate to properties	1
10	Synchtron x-ray	1
11	Take advantage of clay flourescence to image	0
12	SIMS area result (scanning)	0
13	Surface force aparatus	0
14	Catalytic degredation - measure and compare with conventional fillers	0
15	Torsional measurements	0
16	Simulation of Tg	0
17	Control orientation/structure	0
18	Measure mechanism/extent of exfoliation	0

**Nanocomposites -
Technological Needs (29 responses)**

- ■ Characterize degree of exfoliation
- ☐ Dynamics at different time scales
- ▤ Functionalized AFM tips
- ▨ Combining global and local probes
- ▧ Nanomechanics
- ▦ Other (12 topics)
- ▥ Microcalorimetry
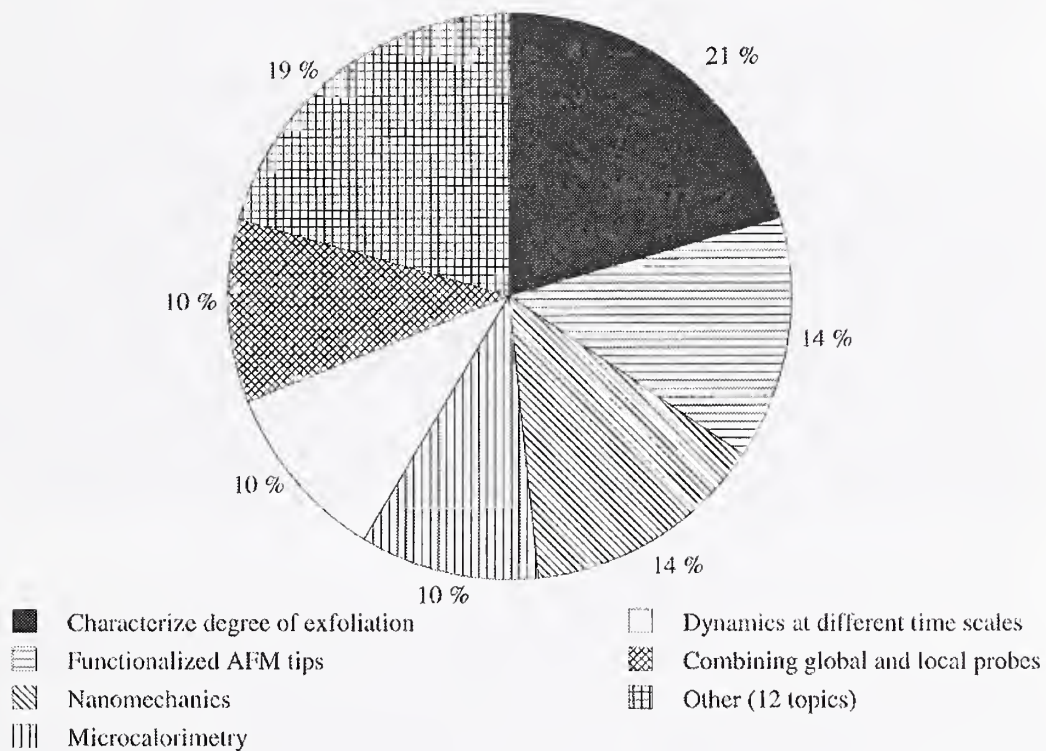
CONCLUSIONS

4.1 Research and Technology Needs

The most important research and technological needs are summarized in the pie charts identified in the previous section. Some general observations are drawn from these results.

Filled Polymers

Research Needs

1. *Characterizing Polymer/Filler Interactions*

The polymer/filler interactions play an important role in the binding and adsorption of molecules at the filler surface, and these interactions determine many of the ultimate properties of filled materials. Control of interaction parameters can be therefore be vital for many filled systems. However, the nature of the polymer/filler interactions is ill-characterized in most filled polymeric systems. This is primarily because of the difficulty in applying measurement techniques suitable for filled polymer systems. Studies on model filler surfaces may be useful in this regard. Studies of blend phase separation in the presence of fillers using scattering and rheology is an approach being tested by the Blends and Processing Group at NIST. Results indicate that this can be used to characterize *relative* polymer/filler interactions in multicomponent filled systems. Absolute characterization of polymer/filler interactions is considerably more difficult, yet all important; an issue that should be addressed in future meetings and workshops.

2. *Dynamics at Filler/Polymer Interface*

While a number of rheological studies exist on measuring the bulk properties of filled systems, there is a paucity of information at the molecular level on dynamics of the polymer chains in filled systems. The volume in the vicinity of the filler is especially important in this regard. As with the polymer/filler interactions, these measurements suffer from technical difficulties in applying straight forward methods to measure local chain dynamics. Nuclear Magnetic Resonance (NMR) is perhaps the most successful technique to date. Inelastic neutron scattering is an equally promising technique for exploring the local chain dynamics in filled systems, especially since the measurements do not require costly deuterated polymers. This program was initiated by the Polymer Blends and Processing Group at NIST for investigating dynamics in nanocomposite materials, and is being extended more generally to filled materials in collaboration with industry.

3. *Surface Chemistry of Fillers (and Silane Coupling Agents)*

Control and characterization of filler surface chemistry is an important industrial approach for modifying polymer/filler interactions. For instance, silane coupling agents are widely used in many applications of filled polymers and therefore of significant interest to the filled polymers industry. Much of the knowledge on the modification and its effect is however at the empirical level. Development of characterization techniques for probing the chemical nature, homogeneity and roughness of the modified surface is deemed important. In addition, the effect of the surface modification in altering

polymer/filler interactions may be key to predicting properties of polymer materials containing surface modified fillers.

Technological Needs

1. *Measurements of transient morphology*

Most current measurement techniques involve measuring only the final state morphology of the filled polymer. However, in order to better control the final state morphology in a typical processing or extrusion, it is important to understand the morphological changes occurring during the different stages of processing. Advances in measurement technology for rapidly measuring transient morphologies is therefore important for the goal of reduction of industrial product development cycles.

2. *Low cost automated technique for dispersion characterization*

Development of an inexpensive technique for characterizing state of dispersion in filled polymers was a unanimous request by the fillers workshop participants. This would involve not only measuring the sample in its dispersed state, but also to quantify it in terms of useful parameters such as loading level, particle anisotropy, aspect ratio, etc. Development of advanced image analysis techniques in two and three dimensions is expected to be a necessary component to quantify dispersion as well. Mathematical tools and concepts such as Fourier transform of images, already in use by the Blends and Processing Group for quantifying morphology and kinetics during phase separation may possibly be applied to more generally characterize filler particle dispersed state. Due to the large number of parameters characterizing the dispersed state of a typical filler, developing a universal parameter defining dispersion is expected to be a non-trivial task.

3. *Online probes of filler distribution and process monitoring*

Related to the problem of measuring transient morphologies is the more general problem of measuring the in-situ state (such as dispersion, morphology, monitoring coupling agent level, etc.) of the filled polymer. Such in-situ measurements will enable incorporation of more efficient adaptive techniques for on-line process corrections. The use of on-line probes for process monitoring has been an ongoing project within the Blends and Processing Group using ultrasonic probes, and more recently using optical temperature probes with success on regular blends. An extension of these measurements to filled polymer systems would be a useful logical step. The monitoring of opaque filler particles is expected to place constraints on the applicability of the optical probe technique, however.

Nanocomposites

Research Needs

1. *Structure and dynamics in confined media*

The effects of confinement on polymer structure (such as chain dimensions, radius of gyration, isotropy, density etc.) can be significant given that the interlayer gallery spacing between clay sheets has the same order of magnitude dimensions as small molecule

polymer chains. Measurements of the polymer structure in confined media and how their dynamics are affected in intercalated and exfoliated clays versus bulk polymer should eventually be related to the ultimate material properties. Inelastic neutron scattering capabilities are expected to be exceptionally promising in accomplishing this goal. To this end, collaborative efforts are currently being forged with filler producers and manufacturing industries involved in this area of research.

2. *Characterization method for degree of intercalation*

The current most commonly used technique for demonstrating the degree of intercalation of polymer into the clay is transmission electron microscopy (TEM) and to a lesser extent, scattering methods. One of the problems with a technique such as TEM is that it does not readily yield the three dimensional (3-D) structure, but instead only a 2-D slice through an arbitrary plane. The results are therefore often dependent on sample preparation and slicing conditions. A more universal method for characterizing the degree of intercalation in nanocomposites in 3-D would be beneficial to obtain more complete structural information on dispersion in clays, especially since the clay sheets are not necessarily planar but mostly undulating.

3. *Characterization of thin film mechanics*

Many nanocomposite applications are expected to be in the area of thin film coatings, and thus an effort is required to characterize their novel mechanical properties. These novel mechanical properties should arise from the strong degree of anisotropy induced in the system due to the high aspect ratio clay platelets. Their orientation and degree of intercalation may strongly affect the mechanical integrity and stability of the coating. The use of atomic force microscopy (AFM) in conjunction with thin film shearing devices may be required for such characterization.

Technological Needs

1. *Characterize and control degree of exfoliation*

An understanding of the factors (e.g. enthalpic, entropic and geometric) controlling the degree of exfoliation is an important technological requirement for preparing nanocomposites with well defined degree of exfoliation. The importance arises from potential applications that may have requirements from nearly unintercalated state, to intermediate intercalated state, and finally to being in the exfoliated state. Characterization of the degree of homogeneity of the dispersed platelets in macroscopic samples is an additional requirement to fully predict and estimate the properties of bulk nanocomposites.

2. *Nanocharacterization utilizing functionalized AFM tips*

Measurements of interactions of clays with differently functionalized polymers may be simulated by performing AFM studies using tips with attached surface groups of different chemical functionality. Local modulus, friction and surface roughness are some of the measurable properties using the AFM. Development of theoretical models to predict such behavior would have to be developed as part of such an effort.

3. *Nanomechanics-real time measure of fracture, toughness*

The real-time measure of fracture and toughness on a local scale at the size of the clay platelets would yield useful insights into the mechanism governing macroscopic mechanical failure in nanocomposites, and means by which it can be avoided. Since the fracture typically occurs very quickly, measurement techniques such as AFM cannot be applied to do real time studies of fracture mechanics. Localized ultrasonic probes and dielectric spectroscopy approaches may be potentially more useful in this regard.

4.2 Summary and Future Outlook

The workshop discussions clearly suggest that there are significant technological and scientific opportunities in extending our knowledge of filled polymers and nanocomposites at a more fundamental scientific level of description. A steady increase in the demand for filled polymeric materials, yet with flexible or finely tunable and predictable properties, makes it imperative to understand key factors governing filled polymer behavior. Control of *molecular level interactions* and *polymer dynamics* at the filler interface have been identified as the most critical issues in filled polymers and nanocomposites in our workshop. Other important issues relate to developing inexpensive methods for characterizing online and in-situ processing studies, better dispersion control, developing a more universal definition for characterizing dispersion, and nano-characterization of filled material properties. The Polymer Blends and Processing Group at NIST has developed a program to study filled polymer and nanocomposites to address some of the most critical issues, in collaboration with industrial partners. Future efforts will focus on some of the other important issues identified through the workshop.

APPENDICES

Appendix I   Workshop Program Agenda
Thursday June 18, 1998
8:30 Registration, Refreshments
9:00 Welcome and Introduction- Leslie Smith, Director, MSEL
9:10 Outline and Introductions - Eric Amis and Alamgir Karim, NIST Polymers Division

Morning-Compounding, Reinforcement and Toughening (I)
9:30 Gary Burns (Dow Corning)- *Concepts in Rubber Chemistry: The Role of the Filler Particle*
10:15 Break
10:30 Henry Yang (Sid Richardson) - *Filler-Filler, Polymer-Polymer and Filler-Polymer interactions: Effects on Rubber Compounds Physical Properties*
11:00 Saad Khan (NC State)- *Flow-induced Microstructural changes in Filled Polymeric Liquids*
11:30 Moshe Narkis (Technion, Israel)- *Recent Industrial Developments: From Anti-Static Polymers to Artificial Marble*
12:00 Discussion
12:30 Lunch Break (NIST Cafeteria)

Afternoon-Compounding, Reinforcement and Toughening (II)
1:45   Albert Yee (U. of Michigan) - *A Comparative Study of Microstructure and Fracture Behavior of a Conventional Filled Polymer and a Nanocomposite: Possible Roles of Interfacial Constraint*
2:30 Rose Ryntz (Ford) - *Effect of Metallocene Impact Modifiers on Cohesive Strength of Thermoplastic Olefins*
3:00 Break
3:15 Mun Fu Tse (Exxon) - *BIMS Elastomer/Filler Interactions*
3:45 Jay Dias (Exxon) - *Investigations of Filler Polymer Interactions*
4:15   Jo Ann Bice (PPG) - *Evolving Structure/Property Relationships for Precipitated Silica*
4:45 Discussion of Needs and Priorities

Friday June 19, 1998
Morning -Nanocomposites
8:30 Emanuelle Gianellis (Cornell U.)- Structure and Dynamics of Polymer Nanocomposites
9:00 Karl Kamena (Nanocor) - Montmorillonite Clay Structures and Intercalation Chemistries based on Dipole Moment Interactions
9:30 Howard Hanley (NIST) - Dispersion in a Clay Nanocomposite; Application of Radiation Scattering
10:00 Break
10:15 Leon Gilgens (TNO netherlands) -Nano-Composites from Polymers and Layered Minerals

10:45 Ramanan Krishnamurthy (U. Houston) - Rheological Study of Macro and Nano Composites
11:15 Jeffrey Gilman (NIST) - Flammability Studies of Polymer Layered Silicate Nanocomposites
11:40 Robert Ivkov (NIST) - Dynamics of Polymers in Confined Geometries: Inelastic Scattering
12:00 Discussion
12:30 Lunch (NIST Cafeteria)

Afternoon-Theory and Simulations
1:45 C.K.H. Dharan (U. Berkeley) - Effect of Fillers and their Distribution on Composite Properties
2:15 Josef Bicerano and Jack Douglas (NIST) - The "Effective" Properties of Polymer-Filler Mixtures
2:45 Coffee Break
3:00 Anna Balazs (U. Pittsburg) - Modeling the Phase Separation of Polymer Clay Nanocomposites
3:30 Discussion of Needs, Priorities and Future Plans

Appendix II

Final Participants List

Workshop on Interactions of Polymers With Fillers and Nanocomposites

June 18-19, 1998
National Institute of Standards and Technology
Gaithersburg, MD

Eric Amis
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6681
Fax: 301/975-4924
Email: eric.amis@nist.gov

Anna Andrews
Ferro Corp.
7500 E. Pleasant Valley Rd.
Techanical Center
Independence, OH 44131 USA
Telephone: 216/641-8580 ext/ 7912
Fax: 216/524-0518
Email: andrewsa@ferro.com

Joseph Antonucci
NIST
Bldg. 224, Rm. A143
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6726

Anna Balazs
University of Pittsburgh
Chem. Eng. Dept.
Pittsburgh, PA 15219 USA

Mike Balogh
GM
30500 Mound Rd.
Warren, MI 48090
Telephone: 810/986-0862
Fax: 810/986-0817

Kathleen Barnes
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-4671
Fax: 301/975-4924
Email: kathleen.barnes@nist.gov

Joerg Baschnagel
Mainz University
Dept. of Physics
Mainz, GERMANY
Email: baschnag@flory.physik.uni-mainz.de

Gary Beall
NANOCOR Inc.
1500 W. Shore Dr.
Arlington Heights, IL 60000 USA
Telephone: 847/394-8844
Fax: 847/394-9040
Email: gbeal@nanocor.com

Charles Beatty
University of Florida
Dept. of Material Science
Gainesville, FL 32611 USA
Telephone: 352/392-1574
Fax: 352/846-2008
Email: cbeat@mse.ufl.edu

Tia Benson-Tolle
Air Force Research Lab.
2941 P St., Ste. 1
AFRL/MLBC B. 654
WPAFB, OH 45433 USA
Telephone: 937/255-9065
Fax: 937/656-4706
Email: bensonth@ml.wpafb.af.mil

Jo Ann Bice
PPG Industries, Inc.
440 College Park Dr.
Monroeville, PA 15146 USA
Telephone: 724/325-5368
Fax: 724/325-5255
Email: bice@ppg.com

Jozef Bicerano
Dow Chemical Company
1702 Building
Midland, MI 48674 USA
Telephone: 517/636-6980
Fax: 517/638-9623
Email: biceranoj@dow.com

Thomas Blinka
Sealed Air Corporation
7500 Grace Dr.
Columbia, MD 21044 USA
Telephone: 410/531-4483
Fax: 410/531-4462
Email: thomas.a.blinka@sealedair.com

Dr. Robert M. Briber
Univ. Of Maryland
Dept. Of Materials and Nuclear Eng.
2100 Marie Mount Hall
College Park, MD 20742-2155
Telephone: 301/405-7313
Fax: 301/314-9601
Email: rbriber@eng.umd.edu

Janis Brown
AFRL/MLBC
2941 P St., Ste. 1
Bldg. 654
Dayton, OH 45433 USA
Telephone: 937/255-0968
Fax: 937/656-4706
Email: brownjm@ml.wpafb.af.mil

Ken Brown
Ferro Corporation
5001 O'Hara Dr.
Evansville, IN 47711 USA
Telephone: 812/435-2166
Fax: 812/435-2169

Gary Burns
Dow Corning Corporation
Pare Industriel
Zone C
Seneffe B-7180, BELGIUM
Telephone: (32)64-88-84-30
Fax: (32)64-88-85-58
Email: gtburns@dcrn.e-mail.com

Forest Busby
The Dow Chemical Company
433 Building
Midland, MI 48667 USA
Telephone: 517/636-8229
Fax: 517/636-0591
Email: fbusby@dow.com

Brent Butler
NIST Boulder
325 Broadway - Mail Code 838.08
Boulder, CO 80303 USA
Telephone: 303/497-3952
Email: brent.butler@nist.gov

Walter Chappas
DAMILIC Corporation
14670 Southlawn Lane
Rockville, MD 20850 USA
Telephone: 301/251-2960
Fax: 301/251-8591
Email: walter.chappas@damilic.com

Martin Chiang
NIST
Bldg. 224, Rm. A209
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6752

Jim Chou
Dow Chemical Company
2301 Brazosport/ B1470A
Freeport, TX 77541 USA
Telephone: 409/238-2601
Fax: 409/238-0047
Email: cchou@dow.com

Deen Chundury
Ferro Corporation
5001 O'Hara Dr.
Evansville, IN 47711 USA
Telephone: 812/435-2166
Fax: 812/435-2169

Stephen Craig
DuPont
Experimental Station/E328-131
Wilmington, DE 19880 USA
Telephone: 302/695-2331
Fax: 302/695-8412
Email: stephen.l.craig@usa.dupont.com

David Curliss
Air Force Research Lab.
2941 P St., Ste. 1
Bldg. 654
WPAFB, OH 45433 USA
Telephone: 937/255-9078
Fax: 937/656-4706
Email: curlisdb@ml.wpafb.mil

Chris Debbaut
Raychem
8000 Purfey Rd.
Fuquay Varina, NC 27526 USA
Telephone: 919/557-8688
Fax: 919/557-8595
Email: cdebbaut@raychem.com

Hari C.K. Dharan
University of California
Dept. of Mech. Eng.
Berkeley, CA 94720 USA
Telephone: 510/642-4933
Fax: 510/643-5599
Email: dharan@me.berkeley.edu

Beibei Diao
DuPont
Rt 141, E174/205B
DuPont Exper. Station
Wilmington, DE 19880 USA
Telephone: 302/695-8055
Fax: 302/695-4855
Email: diaob@BSVAX.email.dupont.com

Jay Dias
Exxon Chemical Company
5200 Bayway Dr.
Baytown Polymer Ctr.
Baytown, TX 77520 USA
Telephone: 281/834-5255
Fax: 281/834-2678
Email: ajdias@erenj.com

Jack Douglas
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6779
Fax: 301-975-4924
Email: jack.douglas@nist.gov

Cynthia Ebner
Sealed Air Corporation
7500 Grace Dr.
Columbia, MD 21044 USA
Telephone: 410/531-4596
Fax: 410/531-4462
Email: cynthia.l.ebner@sealedair.com

Yona Eckstein
BFGoodrich Co.
9921 Brecksville Rd.
Brecksville, OH 44141 USA
Telephone: 216/447-7520
Fax: 216/447-7335
Email: eckstein@brk.bfg.com

Bruce Eichinger
Molecular Simulations Inc.
9685 Scranton Rd.
San Diego, CA 92121 USA
Telephone: 619/546-5540
Fax: 619/458-0136
Email: bruce@msi.com

Tom Ellis
General Motors R&D
Polymers Dept.
M/C 480-106-216
Warren, MI 48090 USA
Telephone: 810/986-1233
Fax: 810/986-8859
Email: tellis@cmsa.gmr.com

Brett Ermi
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-4356
Fax: 301/975-4924
Email: brett.ermi@nist.gov

Ken Farminer
Dow Corning Corporation
2200 Salzburg Rd.
CO2404
Midland, MI 48686 USA
Telephone: 517/496-1693
Fax: 517/496-4511

Yi Feng
Goodyear Tire & Rubber Co.
142 Goodyear Blvd.
Rm. 360, Research
Akron, OH 44305 USA
Telephone: 330/796-2235
Fax: 330/796-7060
Email: yi.feng@goodyear.com

James Fishburn
GE Corporate R&D
1 Research Circle
K1 4A26
Niskayuna, NY 12309 USA
Telephone: 518/387-4095
Fax: 518/387-5812
Email: fishburn@CRD.GE.com

Emmanuel Giannelis
Cornell University
Materials Science & Engineering Dept.
Ithaca, NY USA

Leon Gielgens
TNO
P.O. Box 595
Eindhoven, 5600 AN,
THE NETHERLANDS
Telephone: +31-40-265-0152
Fax: +31-40-244-8350
Email: gielgens@fpd.tno.nd

Jeffrey Gilman
NIST
Bldg. 224, Rm. B256
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6573
Fax: 301/975-4052
Email: jeffrey.gilman@nist.gov

Sharon Glotzer
NIST
Bldg. 223, Rm. A309
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-5729
Fax: 301/975-5008
Email: sharon.glotzer@nist.gov

John J. Godfrey
Aristech Chemical Corp.
1000 Tech. Center Dr.
Monroeville, PA 15146 USA
Telephone: 412/825-3433
Fax: 412/825-3495
Email: godfreyjj@aristechchem.com

Michael Grah
Michelin R&D Corporation
515 Michelin Rd.
P.O. Box 1987
Greenville, SC 29602 USA
Telephone: 864/422-4735
Fax: 864/422-3505
Email: mike.grah@.michelin.com

Richard Harris
NIST
Bldg. 224, Rm. B258
Gaithersburg, MD 20899 USA
Telephone: 301/975-6688
Fax: 301/975-4052
Email: dick.harris@nist.gov

Erik Hobbie
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6774
Fax: 301-975-4934
Email: erik.hobbie@nist.gov

Alex Hsieh
Army Research Laboratory
AMSRL-WM-MA
Aberdeen Proving Grd., MD 21005 USA
Telephone: 410/306-0698
Fax: 410/306-0676
Email: ahsieh@arl.mil

Robert Ivkov
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-4348
Fax: 301/975-4924
Email: robert.ivkov@nist.gov

Krishnamunthy Jayaraman
Michigan State University
Dept. of Chemical Eng.
Engineering Bldg.
East Lansing, MI 48824 USA
Telephone: 517/355-5138
Fax: 517/432-1105
Email: jayarma@egr.msu.edu

Karl Kamena
Nanocor, Inc.
1500 W. Shure Dr.
Arlington Heights, IL 60004 USA
Telephone: 847/394-8844

Alamgir Karim
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6588
Fax: 301/975-4924
Email: alamgir.karim@nist.gov

Charles Kenney
Aristech Chemical Corp.
600 Grant St.
Rm. 1034
Pittsburgh, PA 15219 USA
Telephone: 412/433-1033
Fax: 412/433-7932
Email: kenneyck@aristechchchem.com

Saad Khan
North Carolina State Univ.
Dept. of Chem. Eng.
Raleigh, NC 27695 USA
Fax: 919/515-3465
Email: khan@eos.ncsu.com

Ramanan Krishnamoorti
University of Houston
Dept. of Chem. Eng.
Houston, TX 77204-4792 USA
Telephone: 713/743-4312
Fax: 713/743-4323
Email: ramanan@bayou.uh.edu

Sai Kumar
Amoco Polymers
4500 McGinnis Ferry Rd.
Alphaketta, GA 30005 USA
Telephone: 770/772-8987
Fax: 770/772-8547
Email: kumar@amoco.com

Benjamin Lee
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-2113
Fax: 301/975-4924
Email: benjamin.lee@nist.gov

Yeong Ching Lin
Integral Chemical Corp.
17 Jen-Chen Rd.
Hsiu-Chiu Industry
Hsiu-chu, TAIWAN
Telephone: 88-635-978-599
Fax: 88-635-978762

Da-Wei Liu
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6735
Fax: 301/975-4924
Email: da-wei.liu@nist.gov

Robert Lochhead
University of S. Mississippi
Hardy St.
Dept. of Polymer Science
Hattiesburg, MS 39406 USA
Telephone: 601/266-4868
Fax: 601/266-5504
Email: robert.lochhead@usm.edu

Kevin Lyons
Symyx Technologies
3100 Central Express
Santa Clara, CA 95051 USA
Telephone: 408/764-2040
Fax: 408/748-0334
Email: klyons@symyx.com

Debora Massouda
DuPont
Experimental Station E323/303B
Wilmington, DE 19880 USA
Telephone: 302/695-8751

Michael McBrearty
CEP
705 Yorklyn Rd.
Hockessin, DE 19707 USA
Telephone: 302/234-8206
Fax: 302/239-4677
Email: mm@cep-corp.com

Norman Moll
Dow Chemical Company
677 Building
Midland, MI 48667 USA
Telephone: 517/636-3748
Fax: 517/638-7347
Email: normmoll@dow.com

David Moll
Dow Chemical Corporation
1702 Building
Midland, MI 48674 USA
Telephone: 517/636-9413
Fax: 517/638-9623
Email: djmoll@dow.com

Cal Moreland
Michelin R&D Corporation
515 Michelin Rd.
P.O. Box 1987
Greenville, SC 29602 USA
Telephone: 864/422-4300
Fax: 864/422-3505

Chris Munzy
NIST Boulder
325 Broadway
Boulder, CO 80303 USA
Telephone: 303/497-5549
Fax: 303/497-5224
Email: chris.munzy@nist.gov

Alan Nakatani
NIST
Bldg. 224, Rm. B210
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6782
Fax: 301/975-4924
Email: alan.nakatani@nist.gov

Moshe Narkis
Israel Institute of Tech.
Dept. of Chem. Eng.
Technion City, ISRAEL
Telephone: 972/48232937
Fax: 972-4-823-0476
Email: narkis@tx.technion.ac.il

Diep Nguyen
PPG Industries, Inc.
4325 Rosanna Dr.
Allison Park, PA 15101 USA
Telephone: 412/492-5459
Fax: 412/492-5588
Email: dnguyen@ppg.com

Tinh Nguyen
NIST
Bldg. 226 Rm. B348
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6718
Email: tinh.nguyen@nist.gov

Marc Nyden
NIST
Bldg. 224, Rm. B258
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-6692
Fax: 301/975-4052
Email: marc.nyden@nist.gov

Don Rivin
U.S. Army
Natick RD&E Center
Natick, MA 01760 USA
Telephone: 508/233-4392
Fax: 508/233-5223
Email: drivin@natick-amed02.army.mil

Rose Ryntz
Ford Motor Company
401 Southfield Rd.
A103
Dearborn, MI 48121 USA
Telephone: 313/621-7648
Fax: 313/621-7648
Email: rryntz@ford.com

Dan Sand
Eastman Chemical Company
P.O. Box 1955
Kingsport, TN 37662 USA
Telephone: 423/229-6808
Fax: 423/229-4558
Email: dansand@eastman.com

Nigel Sanders
Specialty Minerals
9 Highland Ave.
Bethlehem, PA 18017 USA
Telephone: 610/861-3457
Fax: 610/861-3412

Thomas Seery
University of Connecticut
97 N. Eagleville Rd., U-136
Storrs, CT 06269 USA
Telephone: 860/486-1337
Fax: 860/486-4745
Email: seery@mail.ims.uconn.edu

William Simendinger
Raychem
8000 Purfey Rd.
Fuquay Varina, NC 27526 USA
Telephone: 919/557-8688
Fax: 919/557-8595
Email: tsimendi@raychem.com

Dennis Simpson
PPG Industries, Inc.
4325 Rosanna Dr.
Allison Park, PA 15101 USA
Telephone: 412/492-5224

Anant Singh
Triton Systems, Inc.
200 Turnpike Rd.
Chelmsford, MA 01824 USA
Telephone: 978/250-4200
Fax: 978/250-4533
Email: anant@tritonsys.com

Diane Steeves
U.S. Army Soldier Systems
Science & Tech Dir.
Natick, MA 01760-5020 USA
Telephone: 508/233-4320
Fax: 508/233-5521
Email: dsteeves@natick-amed02.army.mil

Benjamin Tang
DOT/FHWA
400 7th St., SW
Washington, DC 20590
Telephone: 202/366-4592
Fax: 202/366-3077

Martin Tant
Eastman Chemical Company
P.O. Box 1972
Kingsport, TN 37662 USA
Telephone: 423/229-2147
Fax: 423/229-4558
Email: tant@eastman.com

Ed Townsend
Aristech Chemical Corp.
1000 Tech. Center Dr.
Monroeville, PA 15146 USA
Telephone: 412/825-3356
Fax: 412/825-3495
Email: townsende@aristechchem.com

Tsung-Yen Tsai
ITRI
321 Kuang Fu Rd.
Section 2
Hsinchu 300, TAIWAN
Telephone: 886-3-573-2479
Fax: 886-3-573-2519
Email: 850335@ucl.itri.org.tw

Mun Tse
Exxon Chemical Company
5200 Bayway Dr.
Baytown, TX 77522 USA
Telephone: 281/834-2457
Fax: 281/834-2395
Email: mun.f.tse@exxon.sprint.com

Mark VanLandingham
NIST
Bldg. 226, Rm. B350
Gaithersburg, MD 20899-0001 USA
Telephone: 301/975-4686
Fax: 301/990-6891
Email: mark.vanlandingham@nist.gov

Brent Viers
University of Cinncinnati
P.O. Box 210172
Dept. of Chemistry
Cincinnati, OH 45221 USA
Telephone: 513/556-9290
Fax: 513/556-9239
Email: viersbd@email.uc.edu

Paul Winston
Michelin R&D Corporation
515 Michelin Rd.
P.O. Box 1987
Greenville, SC 29602 USA
Telephone: 864/422-4090
Fax: 864/422-3505
Email: paul.winston@us.michelin.com

William Winter
SUNY-ESF
121 Edwin C. Jahn Lab
Syracuse, NY 13210 USA
Telephone: 315/470-6876
Fax: 315/470-6856
Email: wtwinter@syr.edu

Kurt Wolske
Aristech Chemical Corp.
1000 Tech. Center Dr.
Monroeville, PA 15146 USA
Telephone: 412/825-3469
Fax: 412/825-3495
Email: wolskeka@aristechchem.com

Henry Yang
Sid Richardson Carbon Co.
4825 N. Freeway
Ft. Worth, TX 76021 USA
Telephone: 817/626-3711
Fax: 817/624-9920
Email: sidrich@metronet.com

Albert Yee
University of Michigan
2300 Hayward St., MSE
Ann Arbor, MI 48109 USA
Telephone: 734/763-2445
Fax: 734/763-4788
Email: afyee@engin.umich.edu